ENVIRONMENTAL CONTAMINANTS

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ST. JOSEPH BAY, FLORIDA

Publication No. PCFO-EC 00-01

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Abstract

The U.S. Fish and Wildlife Service (Service) conducted field work in St. Joseph Bay, Florida, for 2-week periods during each of the summers of 1991, 1992, and 1993. The purpose of the work was to complete a baseline survey of the chemical condition of sediments and some biota within the bay. Sediments were collected from 117 sites and analyzed for grain size and total organic carbon content. A sediment map of the bay was created from that data. The sediment at three locations was analyzed for a suite of chemicals including organochlorine pesticides (OC), total polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH) and metals. Ten-day sediment and interstitial water (pore-water) static renewal toxicity tests were completed for three species, using sediments collected from three locations within the bay. The purpose of the toxicity tests was to assess sediment quality. Measurements of the un-ionized ammonia content of sediment interstitial water were made at 126 sites. Sediments were evaluated for dioxin compounds at six locations. In addition, composite samples of three estuarine species (spotted seatrout, blue crab and brown shrimp) were analyzed for dioxin compounds. The study included a survey of the scientific literature and reports relevant to management of chemical contaminants within the St. Joseph Bay ecosystem.

Results of this evaluation indicate that the deeper bay has sediments composed primarily of silts and clays with significant amounts of total organic carbon. The bay has a very limited capacity to cleanse itself of sediments that become contaminated. Contaminants present at levels of concern, or that warrant further investigation, include: un-ionized ammonia, arsenic, mercury, PAHs, PCBs, and dioxin compounds. Bioaccumulation of dioxin compounds at low levels by three species is documented. Toxicity tests reveal that some sediment areas within the bay are toxic, or somewhat toxic, to test organisms. Recommendations are presented within this report for additional research, industrial actions, county and municipal actions, and ecosystem management.

Keywords: sediment, total organic carbon, un-ionized ammonia, arsenic, mercury, polycyclic aromatic hydrocarbons, PAH, polychlorinated biphenyls, PCB, dioxin, furan, spotted seatrout, brown shrimp, blue crab, toxicity test.

Preface

This report is written primarily for scientific and management purposes. An attempt has been made to present the data in a form which is readily usable by managers who have not had formal training in ecotoxicology. Extensive literature has been reviewed and cited to make clear many of the subtle impacts and complexities of chemical contaminant interactions with fish and wildlife species. The primary objective of the authors has been to make a positive contribution to the management of St. Joseph Bay.

Acknowledgments

Many people played important roles in the completion of this project. To all of them, we are most grateful. We especially thank Dr. Parley Winger of the U.S. Geological Survey - Division of Biological Resources, Athens, Georgia, Field Research Station for his many years of assistance, for providing the basic design for the static renewal toxicity tests, and for his extensive critique of the draft report. For scientific guidance and encouragement, we also thank Dr. Ed Keppner, National Marine Fisheries Service (NMFS), and Drs. Charles Facemire and Donald Schultz, U.S. Fish and Wildlife Service (Service). Finally, thanks to Bob Jarvis, who as always, was there with continuous support.

Many volunteers performed important tasks associated with this project, including cleaning nets and gear, cleanup after the toxicity tests, sorting of fish samples, etc. Their assistance was invaluable. For their many days of work, we thank: Hugh Adkison, Jim Barkuloo, Jill Blue, Charla Boggs, Devona Brim, Carolyn Cannon, Gerry Carmody, Kathleen Chapman, Phyllis Clayton, Dennis Creamer, Shelley DuPuy, Chris English, Frank Finchum, John Foster, Guy Gammill, Laura Gammill, Pallas Gandy, Bill Gandy, Ahjond Garmestani, Kathy Hoffmaster, Keith Hutson, Michael Jordan, Jeff Krepper, Robert McGill, Beth Morford, John Quinta, Ann Rosborough, Guy Santora, Robert Stein, Lloyd Stith, Sally Tidwell, Kennard Watson, and Barbara Zolnoski.

Drafts of this report were reviewed by ALA Environmental, Inc.; Dr. James Harvey, U.S. Environmental Protection Agency (EPA); Dr. Wayne Isphording, University of South Alabama; Dr. Edward R. Long, (NOAA); Mr. Thomas L. Seal, Florida Department of Environmental Protection (FDEP); Dr. Ed Keppner, National Marine Fisheries Service (NMFS); and Dr. Parley V. Winger, U.S. Geological Survey. Their time and assistance was particularly appreciated.

Finally, for their support and advice regarding this project, we thank former Field Supervisor Jim Barkuloo and current Field Supervisor Gail A. Carmody.

Contents

Tables

Figures

Appendices

(Contained in Volume Two)

INTRODUCTION

St. Joseph Bay (bay), located within Gulf County, in northwest Florida, has a total surface area at mean high water of 17,755 hectares (ha.) (43,872 acres). Total volume of the bay is approximately 767.4 million cubic meters (622,387 acre-feet) (McNulty et al., 1972). The waters of the bay are clear and salinities are near full strength seawater (35 parts per thousand) (ppt). Freshwater flow into the bay from adjacent land drainage is low, although some freshwater does enter the bay via the Gulf County Canal (Canal), a constructed waterway that connects the bay with the Gulf Intracoastal Water Way (GIWW). One preliminary estimate of the long-term average annual freshwater flow from the Canal is about 1,740 cubic feet per second (cfs) (ALA Environmental, Inc., 1996). On a daily basis, this inflow would amount to less than one percent (0.56%) of the bay's total volume. By comparison, Apalachicola Bay, a true estuary, has an average inflow of approximately 25,000 cfs and a volume of about 968.3 million cubic meters (785,038 acre-feet) (McNulty et al., 1972). On a daily basis, this inflow amounts to 6.3% of that bay's volume, and creates true estuarine conditions of varying salinity. Because of the minimal freshwater inflow, St. Joseph Bay remains a high salinity coastal lagoon, with some estuarine qualities near the mouth of the Canal. Sediment loading to the bay, a phenomenon related to inflow, topography and terrestrial geologic conditions, is insignificant, and thus St. Joseph Bay has remained quite deep since a rise in sea level flooded the coastal plain approximately 5,000 years ago (Stewart and Gorsline, 1962). The bay contains approximately 6,300 acres of seagrasses, primarily turtlegrass (*Thalassia testudinum*), along with shoalgrass (*Halodule wrightii*) and manatee grass (*Syringodium filiforme*) (McNulty et al., 1972). Because of the marine-like conditions within the bay, this coastal lagoon supports a diverse community of invertebrates and fishes. In 1969, the State of Florida designated a large area within St. Joseph Bay as an Aquatic Preserve (Florida Department of Natural Resources, 1992). All Aquatic Preserves are legally considered Outstanding Florida Waters.

Human development around the bay is moderate. The City of Port St. Joe is located along the eastern shoreline near the mouth of the Canal. Residential development is increasing around the bay and along St. Joseph Peninsula. Major industries located adjacent to the bay, or along the nearby Canal, include a paper mill, two chemical companies, and a coal-handling facility. Commercial fishing vessels and associated fish-processing facilities are also located on the Canal. The City of Port St. Joe operates an Industrial Wastewater Treatment Plant with a permitted discharge into the Gulf County Canal. The point of discharge is located on the south side of the Canal approximately 0.67 kilometer (0.42 mile) above the point where the Canal empties into the bay. The treatment plant consists of two primary clarifiers and a 70-acre facultative lagoon. The plant treats a small amount of municipal wastewater. The majority is industrial process water from the paper mill and wastewater from a chemical company. Discharge volume is about 39.5 million gallons per day (61.2 cubic feet/second) (U.S. Environmental Protection Agency, 1996) (EPA).

For this report, a definition of the term *chemical contaminant* is desirable. Many chemicals such as copper, zinc or some aliphatic hydrocarbons are natural components of the bay ecosystem and are present at biologically acceptable concentrations in water, sediments, and biota. Naturally occurring concentrations of these elements or compounds can be viewed as *environmental chemicals*. However, when human activities release excess quantities of these elements or compounds, they become *chemical contaminants*. In addition, some chemicals have been synthesized specifically as pesticides or industrial compounds (DDT, toxaphene, PCBs, etc.) or are biologically-undesirable by-products of industrial activities (dibenzodioxins, dibenzofurans, etc.). Theses types of compounds, usually referred to as *xenobiotic chemicals*, are not beneficial components of biological systems, and many of these chemicals exert toxic effects at extremely low concentrations. These chemicals are also considered *chemical contaminants*. Chemical contaminants can cause *injury to biota* if they are present in sufficient quantities. The potential impact of chemical contaminants

on the indigenous animals of St. Joseph Bay is a management concern. Sometimes it is not possible or practical to directly demonstrate adverse biological effects because of the nature of the effect or the cost associated with direct determinations. In such cases, tools (such as sediment quality guidelines, toxicity studies, residue analysis, etc.) are used to estimate the type and extent of injury to resources.

TRUST RESOURCES

There are many Service trust resources within the St. Joseph Bay ecosystem. Trust resources include federally listed endangered and threatened species, migratory birds, some marine mammals, and anadromous fishes; i.e., those fish species living in marine waters and moving regularly to freshwater areas to spawn, rest, and feed. Service-owned lands such as national wildlife refuges are also trust resources.

In excess of 130 species of migratory birds use bay area habitats for feeding, nesting, and resting (Appendix 1). These species are protected under the Migratory Bird Treaty Act of 1918 (16 U.S.C. Sec 703-711), and include wading birds, waterfowl, shorebirds, raptors and a variety of neotropical migrants. These birds rely on quality habitats for their survival including the open bay, tidal flats and beaches, salt- and freshwater marshes, swamps, and upland forested and grassed areas.

Several species of animals associated with St. Joseph Bay are protected under the Endangered Species Act of 1973 (as amended; 16 U.S.C. 1531 et seq.), including: the *endangered* green sea turtle (*Chelonia mydas mydas*), leatherback sea turtle (*Dermochelys coriacea*), Kemp's ridley sea turtle (*Lepidochelys kempi*), and wood stork (*Mycteria americana*), and the St. Andrews beach mouse (*Peromyscus polionotus peninsularis*) which inhabits areas of St. Joseph Peninsula; and the *threatened* bald eagle (*Haliaeetus leucocephalus*), piping plover (*Charadrius melodus*), loggerhead sea

turtle (*Caretta caretta*) and Gulf sturgeon (*Acipenser oxyrinchus desotoi*). Endangered Florida manatee (*Trichechus manatus latirostris*) occasionally visit the bay. Appendix 2 is a complete list of all endangered, threatened, and candidate species likely to occur in Gulf County, as well as habitats important to these species.

Under the Anadromous Fish Conservation Act of 1965 (16 U.S.C. Sec 757a-757f), the Service also has trust resource responsibilities for anadromous fish, including striped bass (*Morone saxatilis)* and Alabama shad (*Alosa alabamae*). These species occasionally occur in the canal and the bay. The threatened Gulf sturgeon is a third anadromous fish species known to use St. Joseph Bay. In November of 1988, a sturgeon previously tagged by the Service, and weighing 17.2 kg (38 lb), was recaptured in Eagle Harbor and then released (Parauka, personal communication).

The St. Joseph Bay ecosystem provides a variety of valuable habitats and myriad numbers of food chain organisms for all of the trust species mentioned above. The ecosystem is viewed by many as one of the most diverse, productive and important natural areas in Florida.

In addition to trust species, the Fish and Wildlife Service owns and manages Pig Island in St. Joseph Bay. The island is a subunit of the St. Vincent National Wildlife Refuge, and provides an undisturbed coastal environment for a variety of trust species and resident species.

MATERIALS AND METHODS

Collection and Evaluation of Sediment Samples

Protocols used for sediment collection and analyses are contained in Appendix 3. Sediment samples were evaluated for particle size distribution and percent total organic carbon (TOC). Samples were collected from 117 sites within the bay. Some sediment samples collected at depths greater than 6.1 meters (20 feet) were also used for chemical analyses, toxicity tests, and pore-water ammonia evaluations. These measurements were restricted to the finer sediments of the deep bay because they were more likely to accumulate and retain chemical contaminants. The shallow-bay sediments were used only for measurements of particle-size distribution and sediment classification.

Sediment samples were obtained using a Wildco model 1725-F10 standard ponar grab (mouth dimensions, 215 mm x 243 mm). For chemical analyses, a composite sediment sample from each site was obtained by combining 150 mg aliquots collected from the center of five separate ponar grab samples. The ponar grab samples were collected 3 meters apart along a transect. Sediment stations and study sites were located using a Sitex Koden 787 Loran C navigation system which was computer-linked with a Lowrance X-16 chart-recording depth finder.

Samples were placed in certified chemically clean 1-liter (L) jars with teflon liners and were stored frozen at -23° C until shipment to analytical laboratories. Particle size and TOC analyses were run for all samples. Complete chemical analyses were run on three samples. Sieve, hydrometer, and TOC analyses for sediment samples were performed by Tierra Consulting, Inc. Sediment for pore-water extraction was collected by ponar grab and placed into pre-cleaned 3.785 L (1 gal) containers (un-ionized ammonia analysis), or 18.9 L (5 gal) containers (toxicity tests), until the containers were filled.

The effects-based sediment quality guidelines developed by Long et al., 1990, were used in this report to interpret the sediment chemical data. These guidelines are interpretive and are not legally established standards or criteria. The guidelines are based on two chemical concentration values - the ERL and ERM (see below for definitions) - which delineate three concentration ranges for a particular chemical. Concentrations below the ERL value represent a *minimal-effects* range; a range intended to estimate conditions in which biological adverse effects would be *rarely* observed. Concentrations equal to and above the ERL, but below the ERM, represent a *possible-effects* range within which effects would *occasionally* occur. Concentrations equivalent to and above the ERM value represent a *probable-effects* range within which effects would *frequently* occur (Long et al., 1995). The two values are therefore defined as follows:

ERL (Effects Range - Low): The lower 10th percentile of the effects data for each chemical.

ERM (Effects Range - Median): The median, or 50th percentile of the effects data for each chemical.

An aluminum/metal ratio normalization test can also be used to determine if metal concentrations are anthropogenically enriched in sediments (Schropp et al., 1990). That test requires that samples be subjected to *total digestion* using hydrofluoric acid. Our samples were analyzed using *strong acid digestion* which releases less than half of the aluminum that is present. Therefore, the aluminum/metal normalization test could not be applied.

Extraction of Sediment Pore-water

Pore-water was extracted as described by Winger et al. (1991). The pore-water extractor consisted of a fused-glass air stone attached by aquarium airline tubing to a sterile Monojet 60 cc luer-tip polypropylene syringe (model 560224). The syringe

provided the vacuum and also served as the collecting chamber for the pore-water. To extract pore-water, several air stones with connected tubing were placed into clean, numbered 3.875 L (1 gallon) polypropylene containers and the containers were filled, on site, with sediment. The ends of the tubing lines were clamped until extraction began to prevent any loss of volatile compounds or exposure to atmospheric gases. Samples were transported to the field laboratory for extraction of pore-water. A vacuum was created by retracting the plunger of the syringe. The plunger was braced in the retracted position by inserting a piece of wood, cut to the proper length, between the end of the syringe and the plunger lip. When full, syringes were emptied into either chemically clean jars (for use in toxicity tests) or into 5 ml viles (filled completely) and capped for measurement of ammonia content.

Measurement of Environmental Parameters

Water temperature was measured with either a laboratory-quality mercury thermometer or with a temperature-sensitive probe attached by cable to a Yellow Springs Instruments Model 54 oxygen meter. Oxygen concentrations were also measured with this meter. Salinity was measured with either a Yellow Springs Instruments Model 33 SCT meter or with an American Optical temperature-compensated refractometer. The pH was measured using either a Hanna Instruments pHep+ with automatic temperature compensation or with a model 91-57B1 triode pH electrode attached to an Orion portable ion selective electrode (ISE) meter (model 290A). The same meter was used with a model 95-12 ammonia electrode to measure total ammonia. Ammonia concentrations were measured within 4 hours of collection and extraction. Ammonia measurements were converted to un-ionized ammonia concentrations based on pH, temperature and salinity of the samples (Bower et al. 1978, Emerson et al. 1975, Thurston et al. 1979).

Toxicity Tests

Static-renewal toxicity tests were conducted on sediments and sediment interstitial water (pore-water) from three sites in St. Joseph Bay and on Treated Lagoon Effluent (TLE) collected at the point of discharge of the City of Port St. Joe's wastewater treatment facility. Specific station locations are described during the discussion of toxicity test results. Test species included: an Atheriniform cyprinodontid fish, the sheepshead minnow (*Cyprinodon variegatus);* a crustacean arthropod, the opossum shrimp (*Mysidopsis bahia*); and a bivalve mollusk, the Florida lucine clam (*Lucina floridana*). All individual test animals were less than five days old prior to commencement of the tests except the clams which were fully developed adults. Newly hatched sheepshead minnows were cultured at the Panama City Field Office laboratory from fish collected at a pristine site in North Bay, St. Andrew Bay, Bay County, Florida. The opossum shrimp were obtained from a commercial supplier. The lucine clams were collected from shallow seagrass beds at Eagle Harbor, St. Joseph Bay, Gulf County, Florida. The sheepshead minnow and the opossum shrimp are recommended acute-toxicity test organisms because they are easily cultured, sensitive to a variety of pollutants, and are generally available throughout the year from commercial sources (**Weber, 1993**). The lucine clam is a common sediment-dwelling bivalve native to St. Joseph Bay.

Toxicity tests were conducted in a 20-foot mobile laboratory set up next to the marina at the St. Joseph State Recreation Area, Gulf County, Florida. Each morning, four 15 L (4 gal) sediment samples were collected by ponar grab from each study site and placed into 19 L (5 gal) high density polyethylene containers that had been thoroughly washed with soap and water and triple-rinsed with distilled water. These containers were permanently marked on the outside and the same containers were used repeatedly at the same station. Fresh TLE was also collected daily and placed into a pre-cleaned 19 L (5 gal) glass container. The same container was used throughout the study for TLE collection.

Syringes used to collect pore-water during the toxicity tests were reused after cleaning, but were *only* used for the same study site, each day. Most 15-liter (L) sediment samples yielded between 0.5 and 1.5 L of pore-water. A total of 9 L of pore-water was required each day to assure a 50% renewal of the test waters. The volume and time required to extract pore-water varied with the number of vacuum devices used and the sediment particle size. Extraction time was longer for fine silt and clay sediments than for those containing a higher percentage of sand. After extraction, pore-water was temporarily stored in pre-cleaned 3.8 L (1 gal) glass jars. The pore-water was allowed to reach test temperatures (23 to 25 degrees centigrade), and gently aerated for approximately 15 minutes. Jar mouths were covered with clean aluminum foil to minimize the loss of volatile compounds.

Ten tests were run for each of the three species. The water tests included: two control waters, the pore-water (extracted from sediment at three locations), and the TLE. Sediment tests included: one control sediment, and sediment samples collected from three locations. Pre-cleaned 250 ml beakers were used as test chambers. To assure statistically adequate replication, 10 test chambers were used for each test. A total of 100 test chambers was required for toxicity testing of each species. The entire multi-species toxicity test consisted of a total of 300 test chambers. For the opossum shrimp and sheepshead minnow tests, five animals were placed in each test chamber (50 animals per test). For the clam test, two individuals were placed in each chamber (20 animals per test). Each test chamber for the sediment toxicity testing received 60 cubic centimeters of sediment covered with 150 ml of control water. For the pore-water and TLE tests, 200 ml of test solution were placed in the numbered chambers. Salinity of all test solutions was adjusted to 34 ppt, the concentration of the pore-water at the study sites in St. Joseph Bay. Prior to testing, all test chambers were washed with detergent and tap water, rinsed in distilled water, submerged in a 10% nitric acid solution; rinsed in distilled water; rinsed in technical grade acetone; and finally, double-rinsed with distilled water.

Two control waters and one control sediment were included in the tests. One control water was obtained from the Gulf of Mexico (GOM control; latitude 30-04-00, longitude 85-42-00) southwest of Shell Island, Bay County, Florida, and had a salinity of 34 ppt. The second control was artificial seawater (IO control) created using synthetic sea salts (Instant Ocean) and distilled water. The control sediment was collected from an uncontaminated source (previously chemically evaluated) from West Bay in St. Andrew Bay, Florida (latitude 30-15-40, longitude 85-46-00).

On a daily basis during the toxicity tests, 50% of the test solutions (pore-water, effluent, and control water) was carefully removed by siphon and replaced with new test solution or control water. In the sediment tests, the control water over each sediment test chamber was aerated and any loss of water due to evaporation was compensated by addition of distilled water. Salinities were monitored regularly and, when necessary, adjusted to the test salinity by introduction of distilled or control water. At a minimum, oxygen was measured in 80 test chambers and pH in 40 test chambers daily. The animals in each test chamber were inventoried daily and survivors and dead animals were counted (dead animals were removed) and recorded. After measurement of the physical/chemical parameters and the completion of the animal inventories, the shrimp and fish were fed five drops of newly hatched brine shrimp concentrate per chamber. The clams were fed 10 drops of concentrated plankton and organic detritus. The clam food was obtained fresh each day from Eagle Harbor, St. Joseph Bay, using a 153 μ mesh, 0.5 meter diameter plankton net.

Statistical analysis of the data followed procedures outlined and described by Weber (1993) using single concentration test procedures. The data were first subjected to an arc sine square root transformation with modification (Bartlett 1937) when the proportion surviving was 0 or 1. The transformed data were tested for normality using Shapiro-Wilk's test. The F test was used to determine equality of variances (Snedecor and Cochran 1980). For samples of equal variance, a one-tailed T test was used to

determine statistical significance at the 5% level. For samples having unequal variances, a modified T test was used (Weber 1993). If the data failed the test for normality, statistical significance was determined using the nonparametric Wilcoxon rank sum test. Standard statistical values were obtained from Rohlf and Sokal (1969).

Collection of Biological Samples

All samples were handled, prepared and stored in accordance with standard operating procedures described in Appendix 4. Three species of marine animals (one fish; two crustaceans) were collected from the bay for analyses of dioxin compounds. Collection sites are presented in map form in the *Results* section of this report. General descriptions of the sites are provided below.

A composite sample (n=10) of spotted seatrout (*Cynoscion nebulosus*) was collected from the west side of the bay, north and south of Eagle Harbor. The fish were collected by rod and reel from the shallow grass flats. Skinless fillets of the trout were analyzed. A composite sample (n=10) of brown shrimp (*Penaeus aztecus*), collected from the center of the bay, was analyzed (whole body) and a composite sample (n=5) of blue crabs (*Callinectes sapidis*) was analyzed (whole body, but with shells removed). The crabs were collected on the east side of the bay, immediately north of the mouth of the Gulf County Canal.

Microtox^{R} Bioassay

Microtox^{R} bioassays[1] (Microbics Corp. 1992) were conducted on sediment pore-water at sites evaluated for un-ionized ammonia content. The Microtox^{R} test measured the reduction of light emission from the test organism, a bioluminescent marine bacterium (Photobacterium phosphoreum) exposed to pore-water samples. Comparisons are made between bacteria exposed to test waters and those exposed to a control blank. The Effect Concentration (EC) was calculated for the inhibition of the bacterium's normal

[1] Mention of products does not constitute endorsement by the U.S. Fish and Wildlife Service.

light production capability by 50% (EC50) and 20% (EC20), respectively. The more toxic the test solution, the greater effect observed and measured (reduction in light emission by the bacterium). The smaller the EC concentrations, the greater the level of toxicity.

RESULTS

Primary Survey Sites

Figure 1 depicts the six primary sediment collection and chemical analyses sites, and the locations of biological collections -- seatrout, crab, and shrimp. Complete sediment chemical analyses and biological toxicity tests were run using sediment and pore-water collected from D3, D6, and F5. Chemical analyses at these sites included: metals, PAHs, OCs, total polychlorinated biphenyls (total PCB), and dioxin compounds (dioxins and furans). Dioxin analysis was also run on sediments from sites B3, B6, and the reference (Ref) site.

Sediment Survey

The objectives of the sediment survey of St. Joseph Bay were to: 1) understand the physical characteristics and particle size distribution of sediments throughout the bay, 2) produce a map depicting major sediment composition in the bay, and 3) document the occurrence and amounts of chemical contaminants associated with selected sediment samples. Sediment samples were collected from 117 sites within the bay. Appendix 6 contains logistical information about the 117 collection sites including: location (latitude/longitude, loran); depth; percent total organic carbon (TOC); percent carbonate carbon; and grain-size analysis (as percent gravel, sand, silt, clay). The sediment-composition map is shown in Figure 2. For comparison, the map prepared by Stewart and Gorsline (1962) is presented in Figure 3.

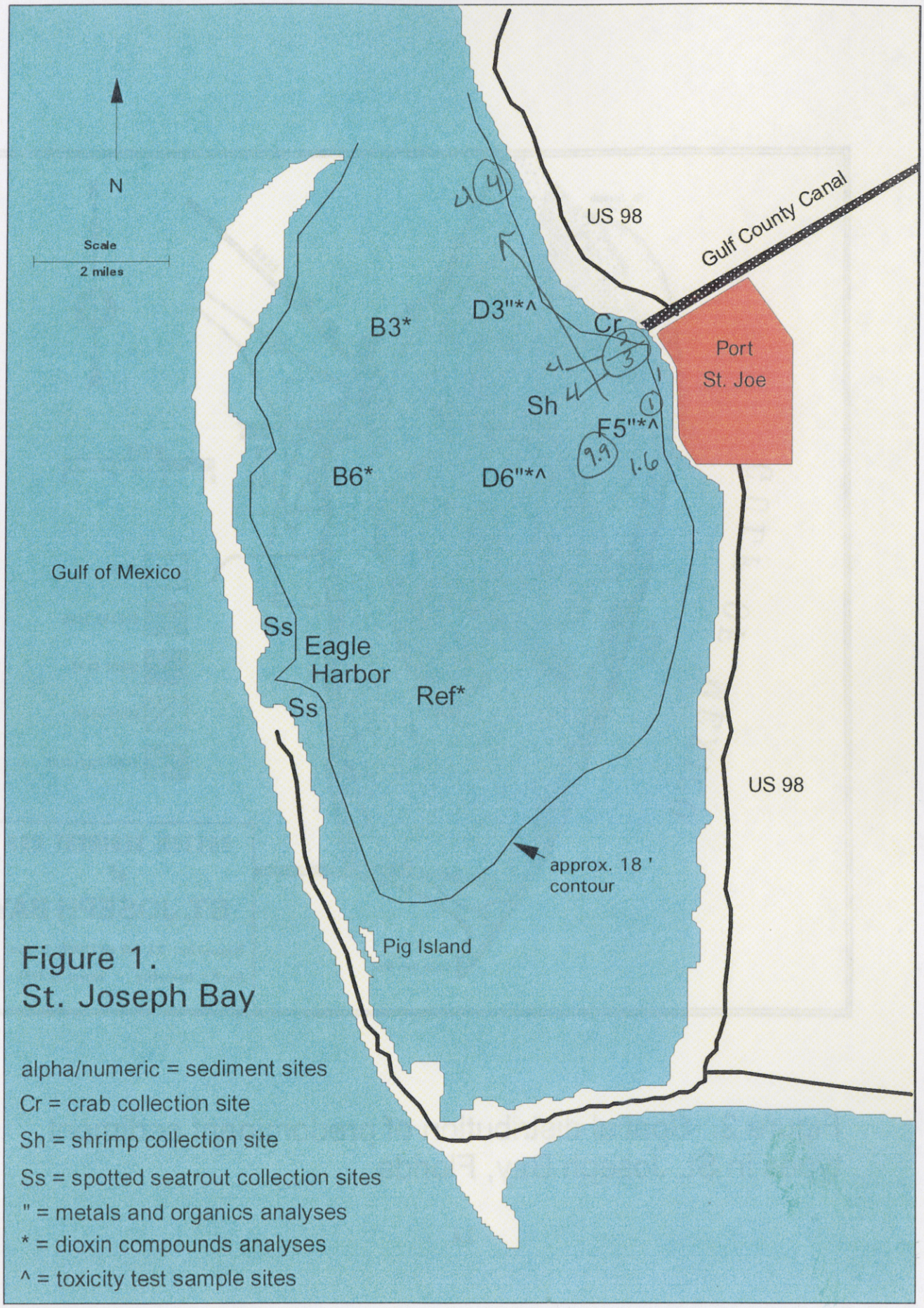

Figure 1.
St. Joseph Bay

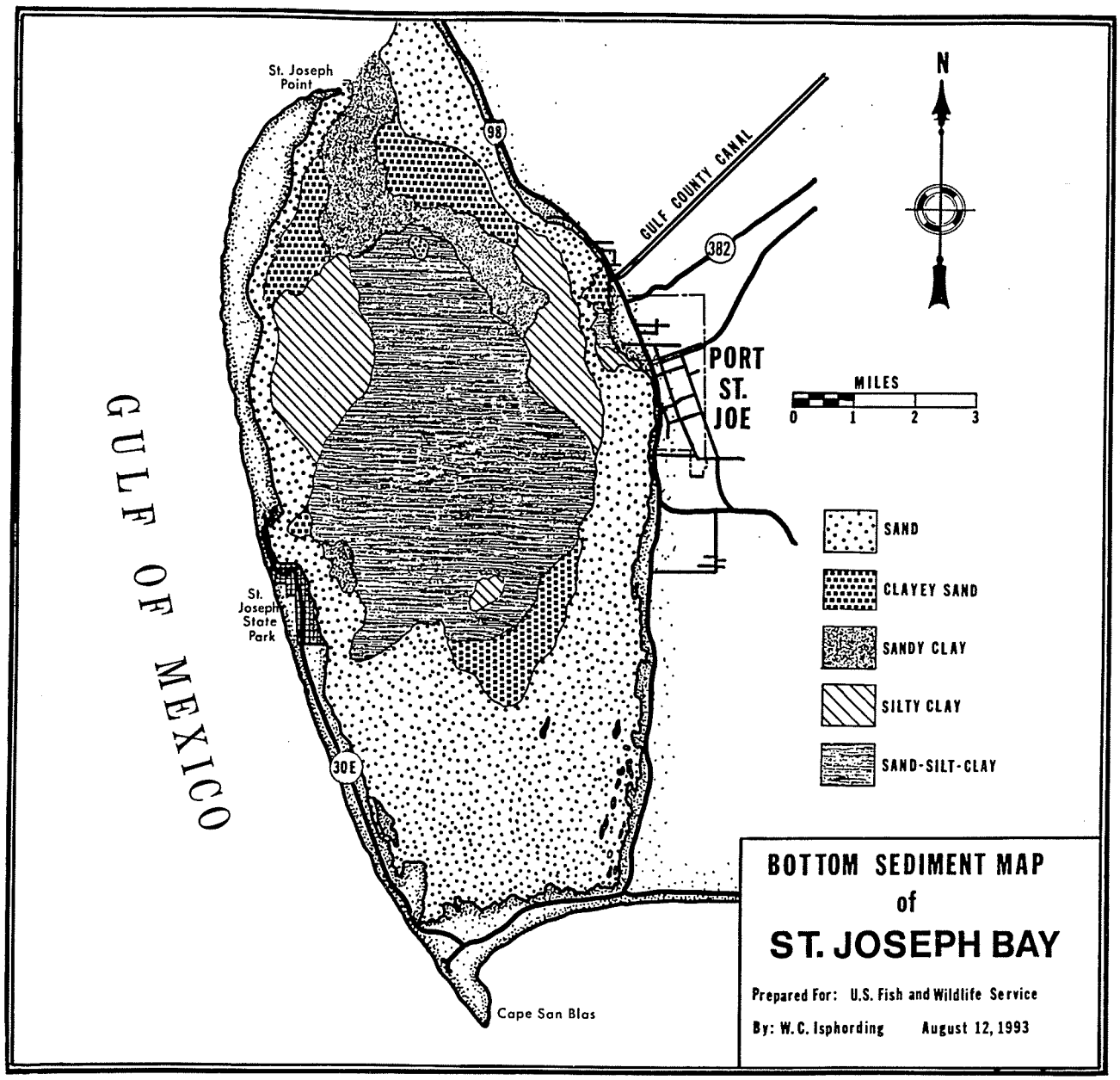

Figure 2. Spatial distribution of predominant sediment types in St. Joseph Bay, Florida

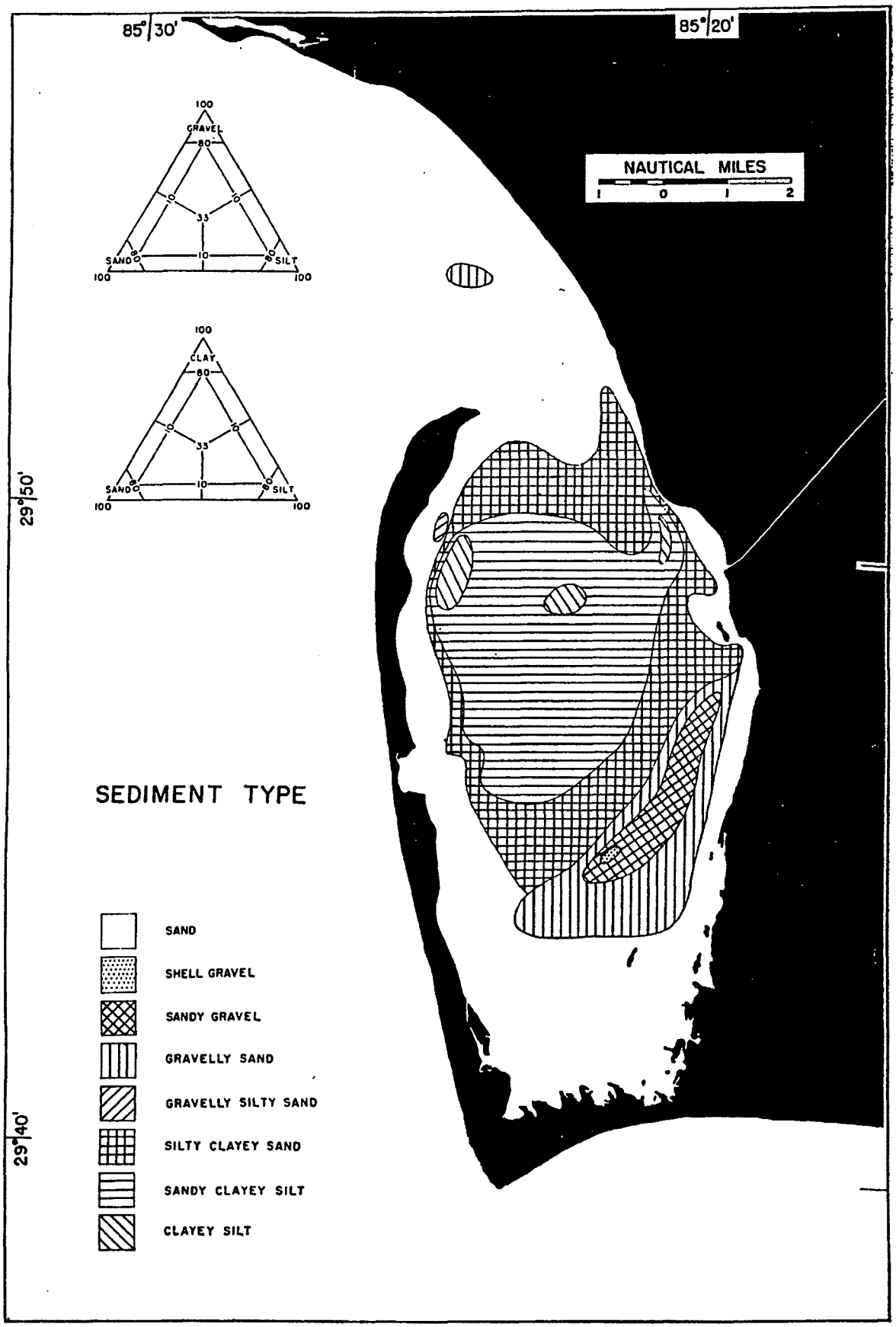

Figure 3. Sediment map of St. Joseph Bay constructed by Richard A. Stewart and Donn S. Gorsline, 1962.

These researchers collected sediment samples from 80 sites, based on a grid dividing the bay into square-mile units oriented north-south (Stewart and Gorsline 1962). Even though the Stewart and Gorsline sediment work was completed nearly 30 years prior to the Service's investigation, and with significantly fewer samples (80 vs 117), the two maps are remarkably similar.

Almost half of the bay consists of sediments of a fine grain nature with dominant amounts of silts and clays. These sediment types are found primarily below the 5.5 meter (18 foot) contour and represent approximately 20,000 acres of deep-water habitat. These sediments are also the most susceptible to contamination by chemicals because they contain high percentages of silts, clays and TOC. For example, there is a very positive correlation between decreasing grain size and increasing trace element concentrations. In addition, the capacity of organic matter to concentrate trace elements in suspended and bottom sediments is well recognized (Horowitz 1991). Invertebrates and fishes dwelling in or upon sediments containing chemical contaminants can accumulate those chemicals, which sometimes results in adverse biological effects (Long et al., 1995).

Stewart and Gorsline (1962) reported that sediments in the area had an average organic content of about 1.4%. This value included shallow and deep estuarine stations. Our evaluation of the TOC content of sediment samples collected at 56 locations in the deeper bay (depths greater than 5.5 meters) revealed an average of 2.35% (range - 0.01 to 5.94%). Percent clay averaged 32% (range - 0% to 62%) and silt averaged 21% (range - 0% to 52%).

Three sediment stations -- D3 (near bay mouth), D6 (center of bay) and F5 (near industrial activities) -- were evaluated for metals, organochlorine compounds, PCBs, PAHs, and aliphatic compounds. The data from these stations provide only a partial view of sediment conditions in the deeper bay. Chemical analyses of additional

samples from other locations would provide a more comprehensive understanding of contaminant loading in the bay.

Except for arsenic and mercury, the concentrations of all metals (for which sediment quality guidelines exist) at the three sites were below effects-range-low (ERL) values (Table 1). Concentrations of arsenic and mercury slightly exceeded the ERL values at stations D3 and D6, meaning that adverse biological effects may occasionally occur to biota utilizing these sediments for habitat or food.

No organochlorine pesticides were detected in bay sediments. Biphenyl concentrations were 32 (D3), 172 (F5) and 265 (D6) μg/kg (ppb), dry weight. No sediment quality guideline for biphenyl is described by Long et al. (1995). The sample concentrations of total PCBs at all three stations exceeded the ERL value of 22.7 μg/kg, dw. Station D6 (283 ppb) even exceeded the ERM value of 180 ppb, above which adverse biological effects frequently occur.

Three PAH compounds exceeded ERL concentrations (Table 2). Acenaphthene exceeded the ERL concentration at the central bay station (D6) and at the industrial station (F5). Fluorene exceed the ERL value at all three stations, and naphthalene exceeded the ERL at F5.

One compound, napthalene, occurred as simple napthalene and in alkylated forms of that compound. Alkylated forms have one to several methyl groups (CH^3) attached to the napthalene molecule. Research (Ott 1978) indicates that methylation of napthalene may increase toxicity of this compound for some species.

The sediment quality guideline concentrations for simple naphthalene are: ERL = 160; ERM = 2,100. Guideline concentrations also exist for one alkylated form, 2-methyl naphthalene: ERL = 70; ERM = 670. Because a smaller amount of the alkylated

naphthalene (2-methyl napthalene) is necessary to produce adverse biological effects, it is probably more toxic than the unalkylated or pure form.

All concentrations of the C1, C2, C3, and C4 naphthalenes and 1,6,7-trimethyl naphthalene (at the three stations sampled) exceeded the ERM for 2-methyl naphthalene of 670 ppb. In addition, 12 out of 15 analyses for these five compounds exceeded the ERM for pure naphthalene of 2,100 ppb. In many cases, concentrations of alkylated naphthalenes not only exceeded these ERM values, but greatly exceeded them (range 2,503 to 18,844 ppb, dw). Because of the locations of the sampling stations, D3, bay mouth; D6, center of the bay; and F5, near industry; it appears that these compounds might be distributed over an extensive area of the deeper bay.

Table 1. Metal concentrations in sediment samples collected from three locations in St. Joseph Bay, Florida, July 1992. Concentrations are mg/kg, dry wt.

Metal	Station D3	Station D6	Station F5
Aluminum	32,400	14,700	10,300
Arsenic	16*	15*	7
Boran	82	22	19
Barium	42	15	13
Beryllium	0.91	1.01	0.36
Cadmium	0.50	<0.20	<0.20
Chromium	46	49	19
Copper	16	15	6
Iron	25,000	23,500	10,500
Mercury	0.165*	0.152*	<0.099
Magnesium	11,700	14,300	5,700
Manganese	418	418	180
Molybdenum	<5	<5	<5
Nickel	16	13	5
Lead	24	19	12
Selenium	1.6	1.7	0.6
Strontium	188	196	301
Vanadium	55	36	18
Zinc	76	61	25

* Value exceeds the "effect range - low" of the sediment quality guidelines (Long et al., 1995).

Table 2. Polycyclic aromatic hydrocarbon (PAH), alkylated PAH, and aliphatic hydrocarbon (phytane) concentrations in sediment samples collected from three locations in St. Joseph Bay, Florida, July 1992. Concentrations are mcg/kg (ppb), dry wt. Compound names preceded with an asterisk have had sediment quality guidelines established.

PAH Compound(s)	Station D3	Station D6	Station F5
*acenaphthene	<10	33*	51*
*acenaphthylene	<10	<26	<18
*anthracene	<10	28	<18
*benzo(a)pyrene	<10	52	19
*chrysene	<10	80	<18
*fluoranthene	19	90	25
*fluorene	39*	213*	140*
*naphthalene	88	118	242*
*phenanthrene	62	217	159
benzo(b)fluoranthene	<10	66	25
benzo(e)pyrene	<10	52	19
benzo(g,h,i)perylene	<10	33	<18
benzo(k)fluoranthene	<10	66	25
dibenzothiophene	180	704	528
indeno(1,2,3-cd)pyrene	<10	38	19
perylene	24	326	51
pyrene	21	104	38
1,2,5,6-dibenzanthracene	<10	<26	<18
1,2-benzanthracene	<10	80	19
1,6,7-trimethyl-naphthalene	783	3,931	2,503
C1-flouranthenes and pyrenes	11	104	19
C1-phenanthrenes and anthracenes	57	302	216
C1-chrysenes	<10	113	19
C1-dibenzothiophenes	229	1,096	898
C1-fluorenes	109	746	408
C1-naphthalenes	870	1,087	3,089
C2-phenanthrenes and anthracenes	60	274	185
C2-chrysenes	<10	80	19
C2-dibenzothiophenes	171	798	637
C2-fluorenes	109	737	401
C2-naphthalenes	3,161	6,757	10,406
C3-phenanthrenes and anthracenes	49	189	108
C3-chrysenes	<10	61	<18
C3-dibenzothiophenes	98	435	287
C3-fluorenes	71	543	267
C3-naphthalenes	6,025	18,744	14,807
C4-phenanthrenes and anthracenes	19	71	45
C4-chrysenes	<10	<26	<18
C4-naphthalenes	4,068	12,720	9,502
phytane	1,596	6,393	9,133

* Exceeds "effects range - low." ** Exceeds "effects range - median."

Toxicity Tests

The toxicity of whole sediment and extracted sediment pore-water was determined from sediment samples collected at three sites (D3, D6, F5) in St. Joseph Bay (Figure 1). In addition, toxicity tests were conducted on treated lagoon effluent (TLE) discharged from the City of Port St. Joe wastewater treatment facility into the Gulf County Canal, and ultimately into St. Joseph Bay.

Station D3 - This station, located near the mouth of the bay (latitude 29-51-00, longitude 85-20-00), was approximately 1.3 kilometers (0.8 statute mile) west of Palm Point and 2.7 kilometers (1.7 statute miles) south of the mouth of the bay. The depth was 8.2 meters. Physical and chemical conditions at this site were significantly affected by tidal currents. The sediment was 6% gravel, 46% sand, 24% silt, and 24% clay.

Station D6 - This station, located near the center of the bay (latitude 29-48-00, longitude 85-20-00), was approximately 4.3 kilometers (2.7 statute miles) west of Constitution Park, City of Port St. Joe. The depth was 9.1 meters. Sediment was 4% sand, 52% silt, and 44% clay.

Station F5 - This station was located in front of the paper mill dock (latitude 29-49-00, longitude 85-18-52) along a line parallel to the dock. Depth was approximately 9.1 meters. This site was selected to evaluate habitat adjacent to industrial activities. Sediment at this site was: 5% gravel, 30% sand, 26% silt, and 39% clay.

Toxicity Test Results

Two tables are used to present the results of the toxicity tests. Table 3 contains survival comparisons between *the field stations* and *the control materials* (water or sediment) for: a) the pore-water and TLE tests, and b) the sediment tests. Table 4

contains survival comparisons *between the individual field stations* for: a) the pore-water and TLE tests, and b) the sediment tests.

Sheepshead Minnow - 10-Day Test

Sediment Pore-water and TLE

Newly hatched sheepshead minnows had an 86% survival rate in both control waters (Table 3). This survival is slightly under the ideal minimum rate of 90% for regulatory decision making (Weber, 1993). There was no significant difference between the survival level in the TLE (82%) and the control waters. Significant differences in survival occurred between the controls and D3 (66%) near the mouth of the bay and D6 (72%) near the center of the bay. The greatest difference in survival when compared to control waters was with the sediment pore-water collected at F5 (survival 0%) near the industrial site. When comparisons were made between the field stations (Table 4), sheepshead minnow survival was significantly greater in the TLE (82%) than in any sediment pore-water. No significant difference in survival was observed between D3 and D6. Survival at station F5 (0%) was significantly less than at all other locations.

Bay Sediments

Survival of sheepshead minnows exposed to the control sediment was 94% (Table 3). No statistically significant difference was observed between control survival and the 80% survival of fish exposed to station D6 sediment. However, survival at stations D3 (76%) and F5 (66%) was significantly lower than the control. When comparisons of survival were made between stations (Table 4), survival was significantly less at F5 (66%) than at either D3 (76%) or D6 (80%). No significant difference in survival was observed between D3 and D6.

Mysid Shrimp - 48-Hour Test

Sediment Pore-water and TLE

Newly hatched mysid shrimp had a 92% survival rate in the Gulf of Mexico control water and an 80% survival rate in the Instant Ocean control water (Table 3). Survival in the IO control was below the ideal minimum rate of 90% for regulatory decision making (Weber, 1993). Survival at station D6 was not significantly less than the controls; however, survival was significantly less at the other field stations compared to controls. When comparisons of survival were made between the stations (Table 4) survival was significantly less at all stations compared to the TLE. At F5 survival was significantly less (0%) than survival at all other stations.

Bay Sediments

The survival of shrimp exposed to the control sediment was 92%. No statistically significant difference in survival was shown between the control and sediments collected at D3 (88%) or D6 (86%) (Table 3). However, survival was significantly lower at station F5 (6%). Comparisons of survival between stations (Table 4) showed no significant differences between stations D3 and D6, but both had significantly greater survival compared with F5 (6%).

Florida Lucine Clam - 10-Day Test

Sediment Pore-water and TLE

Adult lucine clams had a 90% survival rate in the Gulf of Mexico control water and a 100% survival rate in the Instant Ocean control water (Table 3). There was no significant difference in survival between the control waters and pore-water from D3, D6 or the TLE. However, survival of test organisms was significantly lower (10%) when exposed to sediment pore-water from station F5. Comparisons of survival

between stations (Table 4) revealed no significant difference between D3 and D6 or the TLE. Survival at F5 (10%) was significantly less than at the other stations.

Bay Sediments

The survival rate of adult lucine clams exposed to the control sediment was 100% (Table 3). No statistically significant differences existed between survival in the control sediment and any of the three test sediments. Also, no significant differences were observed between individual stations (Table 4).

Table 3. Survival comparisons of test organisms between study sites and controls in St. Joseph Bay, Gulf County, Florida. For each species, survival values with the same superscript are not significantly different ($p < 0.05$).

A. Pore-water or Wastewater Tests

	Stations				Controls	
Test Animal	D3	D6	F5	TLE	GOM	IO
Sheepshead Minnow	66^{a}	72^{a}	0^{b}	82^{c}	86^{c}	86^{c}
Mysid Shrimp	50^{a}	92^{b}	0^{c}	70^{d}	92^{b}	80^{b}
Florida Clam	100^{a}	100^{a}	10^{b}	95^{a}	90^{a}	100^{a}

B. Sediment Tests

	Stations			Control
Test Animal	D3	D6	F5	SAB
Sheepshead Minnow	76^{a}	80^{a}	66^{b}	94^{c}
Mysid Shrimp	88^{a}	86^{a}	6^{b}	92^{a}
Florida Clam	100^{a}	95^{a}	90^{a}	100^{a}

Table 4. Survival comparisons of test organisms between individual study sites in St. Joseph Bay, Gulf County, Florida. For each species, survival values with the same superscript are not significantly different ($p < 0.05$).

A. Pore-water or Wastewater Tests

	Stations			
Test Animal	D3	D6	F5	TLE
Sheepshead Minnow	66^a	72^a	0^b	82^c
Mysid Shrimp	50^a	92^b	0^c	70^d
Florida Clam	100^a	100^a	10^b	95^a

B. Sediment Tests

	Stations		
Test Animal	D3	D6	F5
Sheepshead Minnow	76^a	80^a	66^b
Mysid Shrimp	88^a	86^a	6^b
Florida Clam	100^a	95^a	90^a

Un-ionized Ammonia Sediment Survey

Pore-water Measurements

The un-ionized ammonia concentrations of sediment pore-water samples were evaluated within a primary study area in the vicinity of Port St. Joe and the Gulf County Canal, and at a reference site located between Pig Island and Eagle Harbor (Figure 4). The primary study area was selected for evaluation because it was thought to be potentially influenced by anthropogenic activities. Triplicate measurements were taken at 126 locations at the Port St. Joe site, an area covering 1,889 hectares (4,668 acres). The arithmetic means of those measurements are presented in Figure 5. Triplicate measurements of un-ionized ammonia were also taken at 16 locations within the reference site, an area covering 293 hectares (723 acres) (Figure 6).

Un-ionized ammonia may be the result of natural decomposition processes and not solely from anthropogenic inputs (Sarda et al., 1995). The U.S. Environmental Protection Agency has established ambient water quality criteria for un-ionized ammonia for saltwater aquatic organisms. The Agency states that the majority of these organisms (except for some sensitive species) should not be adversely affected if: 1) the 4-day average does not exceed 0.035 mg/L, more than once every 3 years on the average; and 2) if the 1-hour average concentration does not exceed 0.233 mg/L more than once every 3 years on the average (U.S. Environmental Protection Agency, 1989).

Measurements below the meter's detection limit of 0.1 mg/L occurred at 11% of the sampling sites in the Port St. Joe area. By comparison, 50% of the measurements in the reference area were below detection. At the Port St. Joe area, 89% of the measurements exceeded the 4-day average water quality criterion of 0.035 mg/L. Only 50% of the sites in the reference area exceeded that criterion. However, concentrations within the relatively small rectangular area (40 hectares; 100 acres) adjacent to the industrial site where un-ionized ammonia averaged 2.3 and ranged from 0.3 to 4.7 mg/L ($n=13$) are most likely due to anthropogenic inputs. All of the measurements

within this area exceeded the EPA 1-hour average of 0.233 mg/L. Other measurements from the Port St. Joe study area (n=97), but outside the small rectangular area, averaged 0.25 and ranged from 0.0 to 3.0 mg/L. The average for the reference site was 0.22 and ranged from 0.0 to 0.6 mg/L.

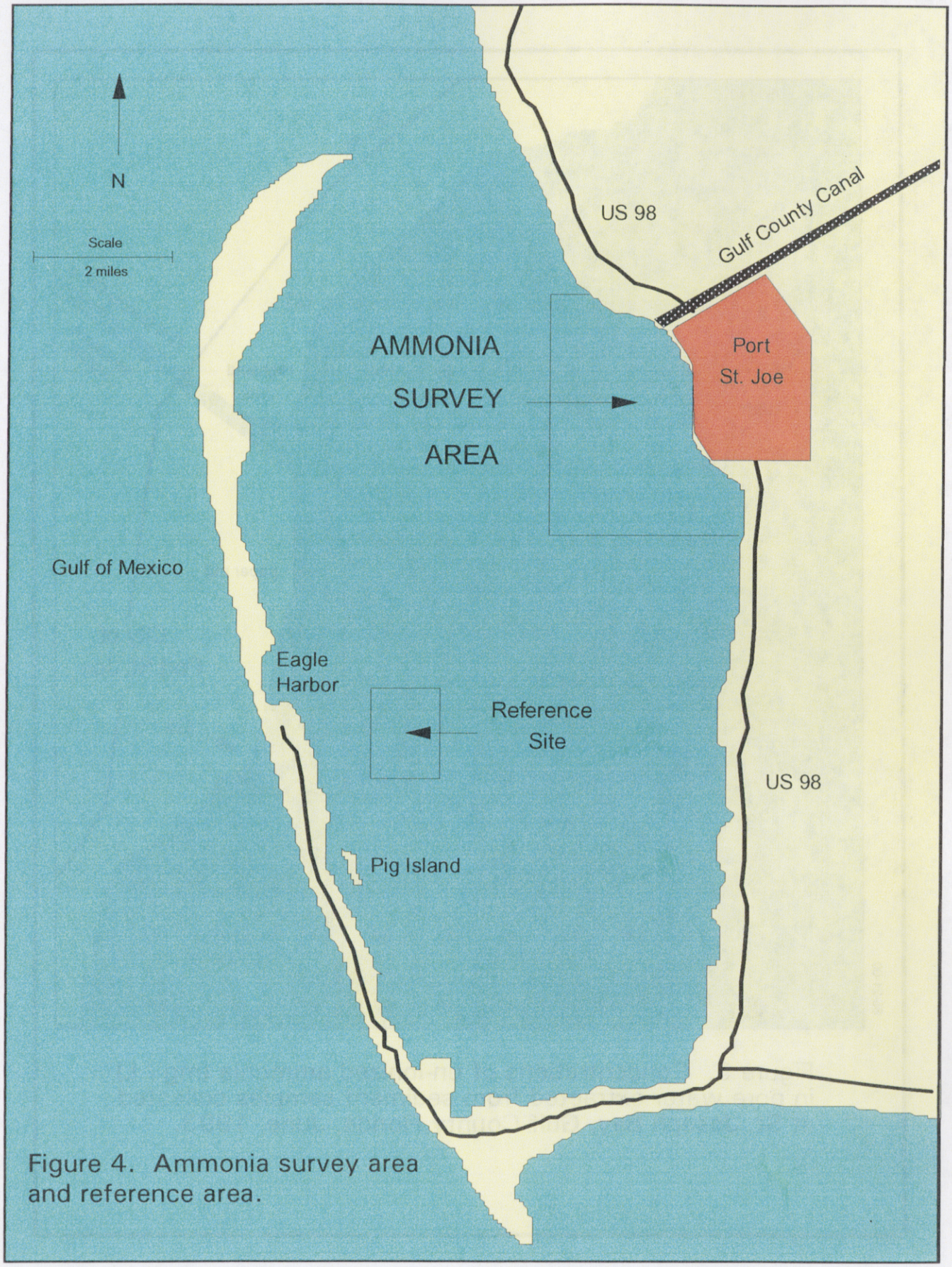

Figure 4. Ammonia survey area and reference area.

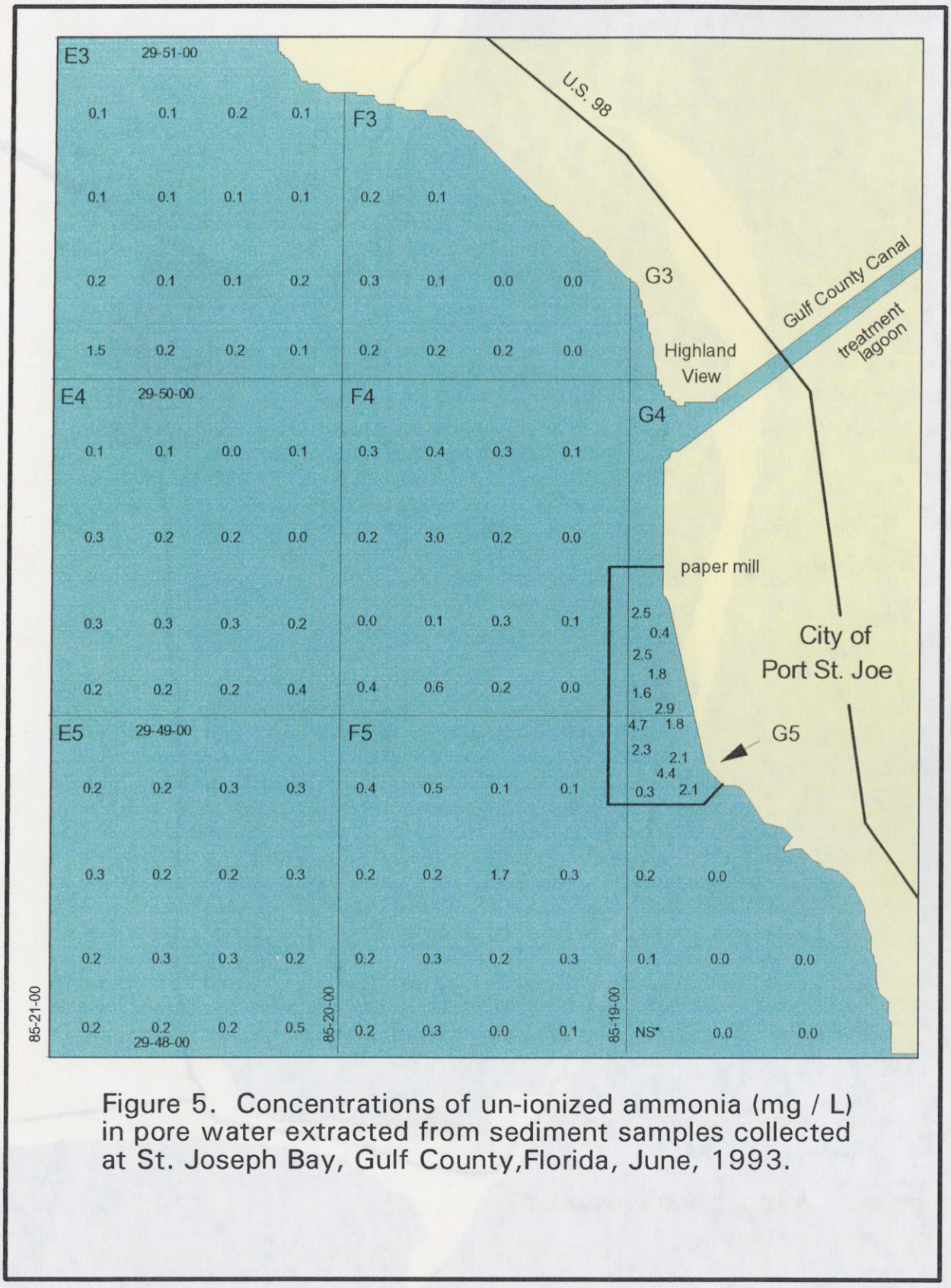

Figure 5. Concentrations of un-ionized ammonia (mg / L) in pore water extracted from sediment samples collected at St. Joseph Bay, Gulf County,Florida, June, 1993.

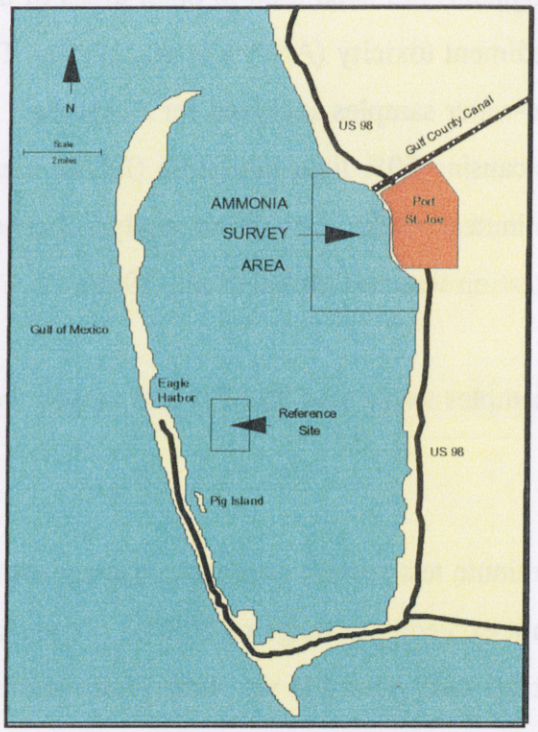

Figure 6. Unionized ammonia concentrations (mg / L) at the St. Joseph Bay reference site.

Reference Site

0.5	0.0	0.4	0.3
0.0	0.0	0.5	0.6
0.0	0.0	0.1	0.6
0.0	0.0	0.0	0.5

Microtox^R Pore-water Evaluation and Un-ionized Ammonia

The Microtox Toxicity Test System^R (System) has been used in other areas of the northern Gulf of Mexico to evaluate sediment toxicity (Ankley et al., 1989). The Microtox^R bioassay was run on all pore-water samples analyzed for ammonia. Effective Concentrations of test waters causing 50% light inhibition (EC50) were obtained for two tests (5 minutes; 15 minutes). Also, correlation analysis between Microtox^R EC50 and ammonia concentration was run (Sokal et al., 1969).

The mean EC50 concentration for all samples tested was 35.02% and ranged from 8 to 99%.

Correlation analysis was run on all 5-minute test results which met quality control standards ($n=31$; confidence interval not exceeding a range of 30%). A significant product-moment correlation coefficient (-0.464; $p>0.01$) was found between the Microtox^R EC50 data (5-minute test) and concentrations of ammonia in the samples tested. These results indicate that some of the observed toxicity may be due to the presence of un-ionized ammonia, but other toxic compounds (possibly metals) are apparently also present.

Correlation analysis ($n=39$) for the Microtox 15-minute test data and ammonia concentrations did not produce a significant product-moment correlation coefficient.

The un-ionized ammonia EC50 for the marine bacteria, *Photobacterium phosphoreum* is 2.002 mg/L (Underwood, personal communication). Because few of the measured concentrations in the St. Joseph Bay sediment were that high, other chemicals are probably exerting some toxic stresses upon these organisms.

EVALUATION OF DIOXIN COMPOUNDS

Introduction

Part of the St. Joseph Bay study included a cursory check to see if dioxin compounds were present in the sediments or biota of the bay. "Dioxin" is a general term for a number of related chemical compounds (polychlorinated-dibenzo-*para*-dioxins or PCDDs) having the same general structure. That structure consists of two benzene rings bonded together by two oxygen bridges (Figure 7, upper). The closely related, and highly toxic, polychlorinated-dibenzofurans (PCDFs) have only one oxygen bridge between the benzene rings. There are 75 potential variations to the molecular structure of dioxins and furans depending on how many, and where, chlorine atoms are attached on each benzene ring (Figure 7, lower).

The attachment positions and the quantity of chlorine atoms on dioxin and furan molecules are factors which determine the extent to which the molecules are toxic (Eisler 1986). Up to eight chlorine atoms can be attached to a dioxin or furan molecule. The most studied, and the most toxic, form of dioxin is the molecule 2,3,7,8-tetrachlorodibenzo-*para*-dioxin; abbreviated 2,3,7,8-TCDD. The numbers in the name refer to the particular positions of attachment for each of four chlorine atoms (U.S. Environmental Protection Agency, 1989).

While 75 types of dioxin or furan molecules are possible, only those molecules with (at a minimum) chlorine atoms at positions 2,3,7, and 8 are toxic. There are 17 such molecules -- 7 are dioxins; 10 are furans. This group of molecules is referred to as the "2,3,7,8-substituted" dioxins and furans; they are the only dioxins and furans of biological interest because they are the only ones which are toxic.

Finally, these seventeen "2,3,7,8-substituted" molecules vary in individual toxicity. Because of the varying degrees of toxicity, a system of relative toxicities has been

developed so that the total toxicity of the group can be determined. This simple system is based on the most toxic molecule: 2,3,7,8-TCDD. It is given a Toxicity Equivalent Factor (TEF) of 1. In any environmental sample, the concentration value of 2,3,7,8-TCDD is therefore multiplied by 1.

Because the dioxins with five chlorines (the pentachlorodioxins) are only half as toxic as 2,3,7,8-TCDD, the concentration of the pentachlorodioxins in any sample is multiplied by 0.5 because half the quantity of the pentachloro dioxins is equal to that same amount of 2,3,7,8-TCDD. As additional chlorine atoms are attached to dioxin and furan molecules, the toxicity decreases, and so does the TEF value. Heptachloro forms are only one-tenth as toxic as 2,3,7,8-TCDD; and their TEF is 0.1. Hexachloros are only one one-hundredth as toxic; their TEF is 0.01. Finally, the octochlorodioxins (8 chlorine atoms) are only one one-thousandth as toxic as 2,3,7,8-TCDD; the octochloro TEF is therefore 0.001.

Dioxin and furan compounds affect living organisms at the cellular and subcellular levels. Rice and O'Keefe (1995) reference many research studies that document the effects of dioxin compounds on aquatic life and wildlife. Dioxin causes cancer in laboratory animals (Lucier, 1992) and is therefore a "carcinogenic" compound, at least to some forms of animal life. Dioxin can also be "teratogenic" (causing defects to developing embryos) (Walker and Peterson, 1992). In addition, dioxin is an estrogenic compound that can adversely affect the endocrine systems of some species, and subsequently may adversely affect embryonic development and even behavioral patterns (Peterson et al., 1992).

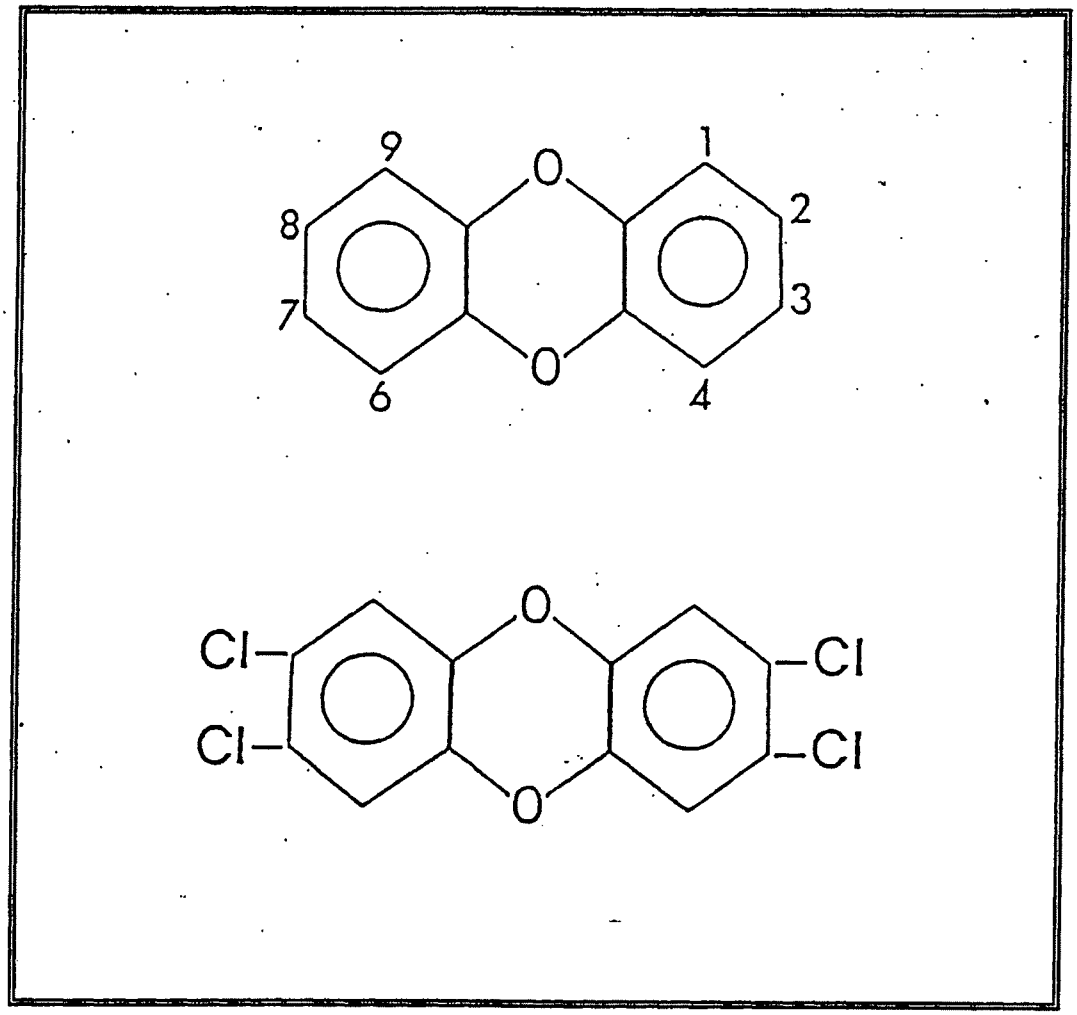

Figure 7. Upper -- Numbering system used for identification of individual PCDD isomers. Lower -- The isomer 2,3,7,8-tetrachlorodibenzo-*para*-dioxin (2,3,7,8-TCDD). From Eisler, 1986.

Sediment Sample Analyses

Composite sediment samples from six locations within St. Joe Bay (see Figure 1) were analyzed for dioxin compounds. The samples were collected during the summers of 1992 and 1993. Dioxin and furan sediment concentrations (of the seventeen 2,3,7,8-substituted isomers) were converted into, and then summed as, toxicity equivalents (TEQs) of the most toxic dioxin isomer: 2,3,7,8-TCDD) (U.S. Environmental Protection Agency, 1989). These summed toxicity equivalents (TEQs) ranged from 2.9 to 10.9 (Tables 5 - 11).

The arithmetic average for the six St. Joseph Bay stations was approximately 8 TEQs. Based on the general uniformity of the dioxin TEQ sums of the six sediment samples, it appears that approximately 8,000 hectares (20,000 acres) of estuarine bottom (that area of the bay deeper than the 6.1 meter/20-foot contour) may be contaminated at concentrations equivalent to about 8 picograms of 2,3,7,8-TCDD per gram of sediment (ppt). Assuming dioxin contamination to a depth of 10 cm (the average depth of the ponar grab sample) as little as 64 to 128 grams of 2,3,7,8-TCDD (or other dioxin and furan isomers equivalent to that amount) discharged or deposited into the bay could account for the concentrations measured during this study.

Larger quantities of some dioxin and furan compounds were present, and although those forms are less toxic than 2,3,7,8-TCDD, their conversion to toxicity equivalents resulted in the average contamination of 8 TEQ. Actually, over a dozen of the more extensively chlorinated dioxin and furan isomers (most of which occurred at much higher numeric concentrations than 2,3,7,8-TCDD) contributed to the observed dioxin/furan contamination of the deep bay sediments. Because our sediment sampling was restricted to depths greater than 6.1 meters (20 feet), statements regarding dioxin contamination are also limited to those depths.

Table 5. Calculation of dioxin TCDD toxicity equivalents for a sediment sample collected at station B3, St. Joseph Bay, Florida, 1993. Concentrations are pg/gm dry wt.

Analyte	PPT	FACTOR	TEQ
2378-TCDD		1	0
12378-PeCDD	1.4	0.5	0.7
123478-HxCDD	3	0.1	0.3
123678-HxCDD	5	0.1	0.5
123789-HxCDD	11.5	0.1	1.15
1234678-HpCDD	120	0.01	1.2
OCDD	1490	0.001	1.49
2378-TCDF	0.97	0.1	0.097
12378-PeCDF		0.05	0
23478-PeCDF	0.40	0.5	0.2
123478-HxCDF		0.1	0
123678-HxCDF		0.1	0
234678-HxCDF		0.1	0
123789-HxCDF		0.1	0
1234678-HpCDF		0.01	0
1234789-HpCDF		0.01	0
OCDF	6.8	0.001	0.0068
		TOTAL 2378-TCDD EQUIVALENTS >	**5.6438**

Table 6. Calculation of dioxin TCDD toxicity equivalents for a sediment sample collected at station B6, St. Joseph Bay, Florida, 1993. Concentrations are pg/gm dry wt.

Analyte	PPT	FACTOR	TEQ
2378-TCDD	0.55	1	0.55
12378-PeCDD	3.3	0.5	1.65
123478-HxCDD	4.9	0.1	0.49
123678-HxCDD	8.1	0.1	0.81
123789-HxCDD	18.1	0.1	1.81
1234678-HpCDD	161	0.01	1.61
OCDD	1670	0.001	1.67
2378-TCDF	2	0.1	0.2
12378-PeCDF		0.05	0
23478-PeCDF	0.87	0.5	0.435
123478-HxCDF	1.4	0.1	0.14
123678-HxCDF		0.1	0
234678-HxCDF	2.1	0.1	0.21
123789-HxCDF		0.1	0
1234678-HpCDF	16.9	0.01	0.169
1234789-HpCDF		0.01	0
OCDF	7.3	0.001	0.0073
		TOTAL 2378-TCDD EQUIVALENTS >	**9.7513**

Table 7. Calculation of dioxin TCDD toxicity equivalents for a sediment sample collected at station D3, St. Joseph Bay, Florida, 1992. Concentrations are pg/gm dry wt.

Analyte	PPT	FACTOR	TEQ
2378-TCDD		1	0
12378-PeCDD		0.5	0
123478-HxCDD	2	0.1	0.2
123678-HxCDD	2.8	0.1	0.28
123789-HxCDD	6.8	0.1	0.68
1234678-HpCDD	75.1	0.01	0.751
OCDD	798	0.001	0.798
2378-TCDF		0.1	0
12378-PeCDF		0.05	0
23478-PeCDF		0.5	0
123478-HxCDF	0.52	0.1	0.052
123678-HxCDF		0.1	0
234678-HxCDF	0.9	0.1	0.09
123789-HxCDF		0.1	0
1234678-HpCDF	5.1	0.01	0.051
1234789-HpCDF		0.01	0
OCDF	4.4	0.001	0.0044
	TOTAL 2378-TCDD EQUIVALENTS >		**2.9064**

Table 8. Calculation of dioxin TCDD toxicity equivalents for a sediment sample collected at station D6, St. Joseph Bay, Florida, 1992. Concentrations are pg/gm dry wt.

Analyte	PPT	FACTOR	TEQ
2378-TCDD		1	0
12378-PeCDD	4	0.5	2
123478-HxCDD	7.3	0.1	0.73
123678-HxCDD	9.9	0.1	0.99
123789-HxCDD	21.6	0.1	2.16
1234678-HpCDD	223	0.01	2.23
OCDD	2150	0.001	2.15
2378-TCDF	2.1	0.1	0.21
12378-PeCDF	0.6	0.05	0.03
23478-PeCDF		0.5	0
123478-HxCDF	1.6	0.1	0.16
123678-HxCDF		0.1	0
234678-HxCDF		0.1	0
123789-HxCDF		0.1	0
1234678-HpCDF	23	0.01	0.23
1234789-HpCDF		0.01	0
OCDF	12.1	0.001	0.0121
	TOTAL 2378-TCDD EQUIVALENTS >		**10.9021**

Table 9. Calculation of dioxin TCDD toxicity equivalents for a sediment sample collected at station F5, St. Joseph Bay, Florida, 1992. Concentrations are pg/gm dry wt.

Analyte	PPT	FACTOR	TEQ
2378-TCDD	0	1	0
12378-PeCDD	0	0.5	0
123478-HxCDD	0	0.1	0
123678-HxCDD	8.2	0.1	0.82
123789-HxCDD	17.4	0.1	1.74
1234678-HpCDD	238	0.01	2.38
OCDD	3060	0.001	3.06
2378-TCDF	3.4	0.1	0.34
12378-PeCDF		0.05	0
23478-PeCDF		0.5	0
123478-HxCDF	3.3	0.1	0.33
123678-HxCDF		0.1	0
234678-HxCDF	4.1	0.1	0.41
123789-HxCDF		0.1	0
1234678-HpCDF	77.3	0.01	0.773
1234789-HpCDF		0.01	0
OCDF	41.9	0.001	0.0419
	TOTAL 2378-TCDD EQUIVALENTS >		**9.8949**

Table 10. Calculation of dioxin TCDD toxicity equivalents for a sediment sample collected at a reference station (Ref), St. Joseph Bay, FL, 1993. Concentrations are pg/gm dry wt.

Analyte	PPT	FACTOR	TEQ
2378-TCDD	0.51	1	0.51
12378-PeCDD	2.5	0.5	1.25
123478-HxCDD	3.3	0.1	0.33
123678-HxCDD	6.8	0.1	0.68
123789-HxCDD	13	0.1	1.3
1234678-HpCDD	126	0.01	1.26
OCDD	1030	0.001	1.03
2378-TCDF	1.8	0.1	0.18
12378-PeCDF	0.53	0.05	0.0265
23478-PeCDF	1.1	0.5	0.55
123478-HxCDF	1.3	0.1	0.13
123678-HxCDF	1.1	0.1	0.11
234678-HxCDF	1.9	0.1	0.19
123789-HxCDF		0.1	0
1234678-HpCDF	14.6	0.01	0.146
1234789-HpCDF		0.01	0
OCDF	8	0.001	0.008
	TOTAL 2378-TCDD EQUIVALENTS >		**7.7005**

Evaluation of Biological Samples

Three marine species collected from St. Joseph Bay were analyzed for dioxin compounds: a) spotted seatrout (*Cynoscion nebulosus*) which are permanent residents of the bay, b) brown shrimp (*Penaeus aztecus*) which inhabit and feed upon organisms associated with the deep sediments of the bay, and c) blue crabs (*Callinectes sapidis*), omnivorous scavengers living in close association with the sediments. Analyses were run for all seventeen 2,3,7,8-substituted dioxin and furan compounds.

Collection sites for the biological samples are identified in Figure 1. An initial attempt was made to collect seatrout from around the mouth of the Gulf County Canal, but not enough fish were obtained for an adequate sample. Therefore, 10 spotted seatrout were collected by rod and reel from the relatively shallow grass flats on the west side of the bay, north and south of Eagle Harbor. A composite sample (n=10) of skinless seatrout fillets was analyzed. Only 2,3,7,8-tetrachlorodibenzofuran was detected in the fillet sample. The concentration was 0.18 pg/gm (ppt) dry weight. Because only fillets (i.e., muscle tissue) were analyzed, no statement can be made about possible dioxin concentrations in reproductive tissues or internal organs.

A composite sample (n=10) of brown shrimp collected from the center of the bay was analyzed (whole body). These shrimp were probably 6 to 12 months old; therefore, the length of exposure time to any dioxin-contaminated sediment would be limited. Two dioxin compounds were detected in these shrimp: 1.9 ppt of octochloro-dibenzodioxin, and 0.14 ppt of 2,3,7,8 tetrachlorodibenzofuran.

Two composite samples of blue crabs (five crabs per sample) were analyzed (whole body, but with shells removed). These crabs were collected on the east side of the bay, immediately north of the mouth of the Gulf County Canal. In the first sample the following dioxin compounds were detected: 1,2,3,7,8-pentachlorodibenzodioxin (0.21

ppt); 1,2,3,6,7,8-hexachlorodibenzodioxin (0.32 ppt); 1,2,3,4,6,7,8 heptachlorodibenzodioxin (0.37 ppt); octochlorodibenzodioxin (1.8 ppt); 2,3,7,8-tetrachlorodibenzofuran (0.39 ppt); and 1,2,3,4,6,7,8-heptachlorodibenzofuran (0.16 ppt).

In the second crab sample (the duplicate sample) the following dioxin compounds were detected: 1,2,3,7,8-pentachlorodibenzodioxin (0.62 ppt); 1,2,3,6,7,8-hexachlorodibenzodioxin (0.52 ppt); 1,2,3,7,8,9-hexachlorodibenzodioxin (0.48 ppt); octochlorodibenzodioxin (3.8 ppt); and 2,3,7,8-tetrachlorodibenzofuran (0.64 ppt).

DISCUSSION

The Potential Fate of Chemicals within the Sediments of St. Joseph Bay

Sediments are an important habitat for hundreds of species of wildlife including marine mammals, birds, sea turtles, fishes, and myriad invertebrates found in St. Joseph Bay. The biological productivity associated with the sediments is of tremendous recreational and economic importance. Therefore, the maintenance of these thousands of acres of sediments in an uncontaminated and productive condition is vitally important to the overall welfare of the St. Joseph Bay ecosystem.

Tidal currents and tidal flushing are both minimal in St. Joseph Bay. Of 37 estuarine study areas on the west coast of Florida, 84% have greater maximum diurnal tidal ranges (McNulty et al., 1972). Atlantic coast U.S. estuaries often have four times the vertical tidal range of the bay.

The sedimentary history and hydrology of the bay provide insight into the probable fate of chemical contaminants entering the system. Prior to the work reported in this study, the only comprehensive evaluation of the sediments of the bay was done in the early 1960's by research scientists at Florida State University (Stewart and Gorsline, 1962). They believe that St. Joseph Bay should more properly be called a lagoon than an estuary because of the lack of significant freshwater inflow. The geologically recent development of the spit (barrier peninsula) over sediments that were deposited from the late Pleistocene to Recent times has created a bay that is basinal in character. More important is the fact that little sediment deposition within the bay has taken place since it was formed by spit development. Comparison of topographic measurements recorded during the 1960's with those made in 1875 and 1841 demonstrate that no appreciable change in depths through the area (bay) has taken place during this 122 - 158-year period (Stewart and Gorsline, 1962).

Because there has been no appreciable change in depth throughout the deep bay, and because there is little freshwater inflow into the system to deliver eroded upland soils, the probability that any existing chemical contaminants will be covered up and confined (isolated) by the influx of soils eroded from uplands is extremely low.

The depth of the bay also precludes any significant chance that contaminated sediments could be eliminated through physical suspension of the sediments into the water column and transport out of the bay. The mild tidal currents of this part of the Gulf are inadequate for such agitation and transport (Isphording, personal communication).

Although continuous shrimping activities within the bay stir up bottom sediments, there is insufficient energy to transport the sediments significant horizontal distances. However, the mixing effect of the shrimp nets along the bottom could explain the apparent homogenous distribution of some chemicals throughout the deeper bay. In fact, Schubel et al. (1979) demonstrated that quantities of suspended sediments (i.e., turbidity) in the trails of nets of commercial shrimp boats were comparable to those observed in the turbid plumes of dredge operations.

Occasionally tropical storms and hurricanes strike the coastline of northwest Florida (Doehring et al., 1994; National Climatic Data Center, 1993 and 1995). In some cases, these storms have power to generate enough energy within some bays and estuaries to disturb and displace contaminated bottom sediments, thereby cleansing these aquatic environments. Isphording (1994) documented the extensive removal of sediments from Apalachicola Bay and Mobile Bay as a result of the energy generated by hurricanes Elena and Frederick, respectively. Elena, in 1985, removed 83 million tons of sediment from Apalachicola Bay, and hurricane Frederick, in 1979, a category 3 storm that made landfall just west of Mobile Bay, caused the removal of 290 million tons of sediment (Isphording et al., 1991). Sediment grain size within Mobile Bay was altered as a result of Frederick, with clay and silt contents significantly reduced. Sediment concentrations of some metals were also reduced.

Although there is potential for hurricane-generated redistribution of contaminated sediments in St. Joseph Bay, the probability of such is low. The average depth of Mobile Bay was approximately 2.3 meters (7.7 feet) (Isphording, 1994), less than one-half the average depth of St. Joseph Bay. Furthermore, the average salinity of Mobile Bay was much less than that of St. Joseph Bay. Isphording's observations in shallow bays are not meant to imply that every hurricane that makes landfall, and even those passing directly over any estuary, will necessarily remove comparable amounts of sediment. Numerous hurricanes have impacted a number of other bays in the northern Gulf of Mexico but have apparently had little effect upon bottom sediments. Examples include historical records for hurricanes that have passed over St. Andrew, Choctawhatchee and Pensacola bays, all of which have remained basically unaffected because they are well protected by extensive barrier island complexes.

Between 1871 and 1936, twenty tropical storms or hurricanes passed within approximately 20 miles of St. Joseph Bay (Appendix 5). Of these, 13 passed over the bay (National Climatic Data Center, 1993 and 1995). But Stewart and Gorsline (1962) found no appreciable change in depth or area since 1841. Apparently hurricanes cannot generate enough energy to agitate bottom sediments deeper than 20 feet which are overlain with nearly full-strength sea water and which are protected by a land barrier such as a spit. Dr. Wayne Isphording (personal communication) believes that it is highly unlikely that hurricanes could mobilize and transport sediments in some north Florida, deep, high-salinity bays, such as St. Joseph Bay or St. Andrew Bay.

Since hurricanes have not transported sediments in appreciable quantities from the bay over the last 156 years, chemical contaminants discharged into the bay, and associated with sediments deeper than 20 feet, are likely to remain there, unless they are degraded by biological organisms or incorporated into, and moved up, the biological food chain.

Biological Significance of Chemical Contamination Documented within the Bay

This study, within limits, has characterized the extent and type of chemical contamination of the sediments of the deeper portions of St. Joseph Bay. Contaminants of concern include un-ionized ammonia, some metals (arsenic and mercury), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and dioxin compounds.

A. The Sediment Survey - Potential for Biological Impacts

The results of the sediment survey reveal that St. Joseph Bay has a large area, in excess of approximately 20,000 acres, below the 6.1 meter (20-foot) contour, consisting of sediments with high percentages of silt, clay and total organic carbon. These sediments were apparently deposited thousands of years ago, and are not of recent origin. Such sediments can quite easily accumulate chemical contaminants, and contaminants associated with these sediments can be accumulated by biological organisms inhabiting the bay.

B. Toxicity Tests

Most contaminants that enter aquatic systems are ultimately deposited in the bottom sediments (Salomons et al., 1987). To have a toxic effect on aquatic organisms, contaminants must be biologically available. In aquatic systems, the major route of exposure is solution (Winger et al., 1991). However, to produce a toxic effect, the quantities of contaminants in the sediments have to be sufficiently high for the equilibrium-partitioning concentration in solution to exceed toxic levels (Adams et al. 1985; O'Donnell et al., 1985). The solution phase of any sediment is the water which fills the spaces between the sediment particles, and is referred to as *pore-water* or *interstitial water*. Therefore, assessing the toxicity of sediment pore-water is an important and logical step in evaluating sediments and the bioavailability of contaminants contained within them (Winger et al., 1991). The complexities of

collecting and handling pore-water are described in detail by Adams (1991). Ideally, in any evaluation of sediment pore-water, the goal is to evaluate the toxicity associated with the original *in situ* chemical forms of elements and compounds of concern. Alteration of those forms can take place, usually through oxidation, or evaporation of volatile compounds. If such alteration takes place, the original toxicity is usually reduced and toxicity values are under-estimated. Our test solutions had to be oxygenated because of the significant biochemical oxygen demand (BOD) of the sediment. Thus both oxidation and evaporation may have mitigated the toxic strength and effects of some compounds. An attempt was made to minimize these problems by replacing one-half of the test solution each day, with freshly extracted pore-water.

Multi-species toxicity tests indicated that pore-water associated with some sediments was acutely toxic. This toxicity was greatest near station F5, where survival never exceeded 10%. Toxicity was also associated with pore-water in sediment at station D3. Minor toxicity was observed in tests of the TLE, but was restricted to the most sensitive species tested, the mysid shrimp. No appreciable acute toxicity was observed in tests of pore-water from the center of the bay (D6). Whole sediment tests generally resulted in lower levels of mortality than the pore-water tests. However, the sediment at station F5 was toxic to sheepshead minnows and very toxic to mysid shrimp.

These tests indicate that there has probably been some net loss in the biological diversity and productivity of St. Joseph Bay associated with deep sediment habitat in some areas. Sediment sample chemical concentrations which exceeded sediment quality guidelines also support this probability. Although several chemical contaminants may have contributed to the observed toxicity, the chemical most likely to have adversely affected the biota was un-ionized ammonia (see next section). However, out in the bay, oxygen depletion caused by excessive historic discharge of organic materials into the bay may also have degraded the deep water habitat. In addition, excess formation of hydrogen sulfide may render some sediment areas toxic.

C. Un-ionized Ammonia in Sediment Pore-water

Ammonia (including the ionized form, NH_4^+; and the un-ionized form, NH_3) occurs in the environment as a result of natural processes as well as from human activities. "Total ammonia" is the sum of the concentrations of both forms of ammonia. A key intermediate in nature's nitrogen cycle, ammonia concentrations are in dynamic equilibrium with existing chemical conditions. Elevated concentrations of ammonia are usually the result of anthropogenic activity (U.S. Public Health Service, 1989).

Un-ionized ammonia (NH_3) is one of the most important pollutants in the aquatic environment because of its toxic nature and its ubiquity in surface water systems (Russo, 1985). Under aerobic conditions, un-ionized ammonia is oxidized to nitrite (NO_2^-) by one species of bacteria (*Nitrosomonas*). Nitrite is then oxidized to nitrate (NO_3^-) by a second species of bacteria (*Nitrobacter*). Nitrate is considerably less toxic to aquatic organisms than are un-ionized ammonia and nitrite (Russo, 1985). If un-ionized ammonia does not undergo oxidation, it accumulates in the aquatic environment and can have acutely toxic effects on marine organisms. Un-ionized ammonia in the interstitial water (pore-water) of sediments can be toxic to sediment dwelling fish and invertebrate larva as well as adult organisms. Factors that affect the toxicity of un-ionized ammonia include temperature, pH, salinity, and dissolved oxygen (Russo, 1985). As water temperature increases from 0^0 to 30^0 C, the amount of un-ionized ammonia increases. However, temperature does not increase un-ionized ammonia concentrations as significantly as do changes in pH (Rattner and Heath, 1995; Emerson et al., 1975). Fortunately, pH in marine systems fluctuates little and is relatively stable.

Currently, the State of Florida has an un-ionized ammonia water quality criterion for the protection of fish and wildlife for Class III waters, which are predominantly marine systems. Pore-water associated with sediment habitats has not been viewed as distinct from the overlying water column. For marine systems, for the protection of fish and

wildlife, the criterion states that un-ionized ammonia concentrations shall not exceed 0.035 mg/L (Florida Administrative Code, Chapter 62-302.530). Acute toxicities reported for ammonia in the marine environment range from 0.5 mg/L to 19.1 mg/L (U.S. Environmental Protection Agency, 1989).

The EPA, in its report on the ambient water quality criterion for un-ionized ammonia under the Federal Clean Water Act, states that:

> "except possibly where a locally important species is very sensitive, saltwater aquatic organisms should not be affected unacceptably if:
>
> > The *four-day average* concentration of un-ionized ammonia shall not exceed 0.035 mg/L more than once every three years on the average and if,
> >
> > The *one-hour average* concentration does not exceed 0.233 mg/L more than once every three years on the average." (U.S. Environmental Protection Agency, 1989)

The pore-water of the sediments in the deeper portions of the bay is lower in oxygen than is the overlying bay water, a situation which could increase un-ionized ammonia toxicity. Ammonia is frequently associated with a reduction of oxygen levels in the receiving water. This is brought about by several causes, including the oxygen demand of the ammonia as it is converted by natural microbial oxidation to nitrite and nitrate (Russo, 1985). Several researchers, working with a variety of fish species, have reported that the toxicity of ammonia increases when dissolved oxygen concentrations decrease (Russo, 1985).

Ammonia has deleterious effects at fairly low concentrations which are not high enough to cause death (Russo, 1985). In long-term tests, fish exposed to low concentrations (0.002-0.15 mg/L) exhibited the following: reduced food uptake and assimilation, growth inhibition, histological changes, swelling, diminished number of red blood cells, inflammation and degeneration of gills and kidneys, and lowered resistance to disease (Russo, 1985; Flis, 1968; Smart, 1976; Thurston et al., 1978). Not enough data are available from chronic or sub-chronic studies to provide definitive information on whether such factors as pH, acclimation, dissolved oxygen, and salt concentration, which have demonstrated effects on acute toxicity, also affect chronic toxicity (Russo, 1985).

Ammonia in sediments has been linked to declines in aquatic life. Studies with fingernail clams (*Musculium transversum*) demonstrated that declines of that species in the Illinois River were related to the presence of ammonia in sediment interstitial water. The ammonia inhibited the cilia and filtering ability of the clams (Upper Mississippi River Conservation Committee, 1992). In a study at Brunswick Estuary, Georgia, Winger et al. (1993) reported sediment pore-water concentrations of un-ionized ammonia from 0.07 to 0.10 mg/L. However, pore-water from sediments in the polluted Fox River, Wisconsin, ranged from 1.3 to 4.4 mg/L un-ionized ammonia (Ankley et al., 1990).

Un-ionized ammonia is discharged in large quantities in industrial, municipal and agricultural wastewaters (Russo, 1985). Ammonia can be released from paper mills that utilize ammonia as the base for the pulping chemical in the ammonium sulfite process. Ammonium-base sulfite pulp, however, is only a fraction of all the pulp produced in the United States (Springer, 1986). Ammonia in paper mills can be controlled by substitution to a different base chemical or through the application of biological treatment that allows nitrification of ammonia (U.S. Environmental Protection Agency, 1980).

Historically, paper mill effluent was discharged directly into St. Joseph Bay, but by the late 1970's, treatment was accomplished by a municipal wastewater treatment lagoon operated by the City of Port St. Joe. Under the current National Pollutant Discharge Elimination Program (NPDES) permit (effective October 1, 1994), there is no effluent limitation, nor any monitoring requirement, for un-ionized ammonia that might be contained in effluent released from the City's wastewater treatment facility (U.S. Environmental Protection Agency, 1994).

In summary, un-ionized ammonia within the pore-water of deep sediments in St. Joseph Bay is present over the large area sampled and exists at concentrations which are often an order of magnitude greater than the Florida and EPA water quality criterion for the four-day average ammonia concentration (0.035 mg/L) established for marine waters. Some areas had sediment pore-water ammonia concentrations which would be acutely toxic to some marine organisms.

D. Metals in Bay Sediments

Several metals may be acutely toxic at extensively degraded sites. However, these contaminants are probably more important as sources of chronic toxicity at less degraded sites where they may be incorporated into food chain organisms, biomagnified up the food chain, and taken up by predator species.

ARSENIC

While the levels of arsenic in two of three sediment samples were almost double the ERL value, these results should not be interpreted as indicative of an environmental problem. The results simply indicate that other additional sampling for arsenic is desirable. Furthermore, low levels of arsenic (in a variety of forms of arsenic compounds) normally occur in many marine animals. In a study in Perdido Bay, Florida, (Brim, 1993) arsenic levels in gafftopsail catfish ranged from 1.2 - 10.6 mg/kg, wet weight. These values are normal for marine fishes. It is thought that

arsenic is often elevated in marine biota because of their ability to accumulate this element from seawater or food sources (Maher, 1985). At this time, there is no evidence to indicate that the observed arsenic values detected in the sediments of St. Joseph Bay are due to localized pollution. The great majority of the arsenic in marine organisms exists as water-soluble and lipid-soluble organoarsenicals. For most marine species there is general agreement that arsenic exists primarily as arsenobetaine, a water soluble organoarsenical that poses little risk to the organism or its consumer (Eisler 1988).

MERCURY

Mercury contamination in Florida has been a concern since elevated levels were documented in some freshwater systems in 1982 (Bigler et al., 1985). In 1989, the State of Florida assembled the *Mercury in Fish and Wildlife Task Force* to investigate and evaluate the problem of mercury contamination State-wide. As a result of the State's mercury investigation, in 1989, fish consumption health advisories were formulated (Florida Department of Health and Rehabilitative Services, 1993). Given the various contemporary global and regional sources of mercury, it is prudent to monitor concentrations of this metal in all Florida environments.

Mercury and its compounds have no known normal metabolic function. The presence of mercury in cells of living organisms represents contamination from natural and/or anthropogenic sources. Any such contamination should be regarded as undesirable and potentially hazardous. Some forms of mercury with relatively low toxicity can be transformed into forms with very high toxicity through bacterial methylation and other biological processes. Methyl mercury, taken up from sediments, can be bioconcentrated in organisms and biomagnified through food chains to upper trophic level consumers. In organisms near the top of the food chain, such as carnivorous fishes, almost all mercury accumulated is in the methylated form, primarily as a result of the consumption of prey containing methyl mercury (Eisler, 1987).

Mercury has mutagenic, teratogenic and carcinogenic properties, and has caused embryocidal, cytochemical and histopathological effects. At comparatively low concentrations, reproduction, growth, behavior, metabolism, blood chemistry, osmoregulation, and oxygen exchange are adversely affected in marine and freshwater organisms. In general, the accumulation of mercury by aquatic biota is rapid, and depuration is slow (Eisler, 1987).

Some of the human activities that have contributed significantly to the environmental contamination by mercury include combustion of fossil fuels, disposal of batteries, production of electrical equipment, industrial instruments (thermometers, and barometers, etc.), marine anti-fouling paints, chemical formulations to control fungal diseases, and pulp and paper processing. Historically, mercury preservatives were added to wood pulp to prevent the growth of slime; however, in the United States mercury slimicides were banned in 1965 from wood pulp used to make paper products which would come into contact with food (D'Itri et al., 1977).

Mercury concentrations, in two of the three sediment samples from the bay, were barely above the ERL value. However, because of the limited number of sediment samples collected, additional samples should be evaluated. Because of the significant capacity of organisms to biomagnify methyl mercury in their tissues, analysis of biological samples is also desirable.

E. Polycyclic Aromatic Hydrocarbons (PAHs)

Several PAH compounds are among the most potent carcinogens known to exist, producing tumors in some organisms through single exposure to microgram quantities. Current aquatic research has focused on PAHs because of their known relationship with carcinogenesis and mutagenesis (Eisler, 1987). PAH are components of crude and refined petroleum and of coal. Oil spills are a major source of PAH in freshwater and marine environments (Neff, 1985).

In this study, concentrations of acenaphthene, fluorene, and naphthalene all exceeded ERL levels at one or more of the sediment stations that were sampled. Furthermore, many alkylated PAH compounds (PAH ring structures with carbon branches attached), particularly alkylated napthalenes, were detected in sediment samples in concentrations that ranged up to nearly 19,000 parts per billion (ppb). There is evidence that increased alkylation of some PAH compounds (example - naphthalene) increases the toxicity of these compounds to aquatic organisms. For example, Ott (1978) exposed a marine amphipod (*Eurytemora affinis*) to simple naphthalene and various alkylated forms of naphthalene. The *LC50* is defined as the concentration (amount) of the chemical in water that kills 50% of the test organisms. When naphthalene was tested, the LC50 amount *decreased* as alkylation *increased.* Concentrations required for LC50 mortality (in microgram quantities per liter of water; i.e. ppb) were as follows: simple naphthalene (3,800 ppb); 2-methylnaphthalene (1,500 ppb); 2,6-dimethylnaphthalene (900 ppb); and 2,3,5-trimethylnaphthalene (300 ppb). As more carbon side-branches were attached to naphthalene, less of the chemical was required to kill 50% of the test animals.

The sediment quality guideline ERL and ERM concentrations for naphthalene are 160, and 2,100 ppb, dry weight, respectively; but alkylization to 2-methylnaphthalene reduces these sediment concentrations to 70 and 670 ppb (Long et al., 1995). Less than half as much of the alkylated form is required to produce the same adverse results to biota. Thus, alkylation does increase toxicity.

The total concentrations of alkylated naphthalene (sum of C1+C2+C3+C4 forms) in the three sediment samples from St. Joseph Bay were as follows:

Station D3 - 14,124 ppb
Station D6 - 39,308 ppb
Station F5 - 37,804 ppb

These values greatly exceed the sediment quality guidelines. Given the potential impacts from PAHs at concentrations measured in the bay, further evaluation of the potential adverse affects of these compounds is warranted.

F. Total Polychlorinated Biphenyls (PCBs)

PCBs exceeded the ERL concentration (22.7 ppb) at all stations sampled in the bay. At station D6 the concentration of PCBs detected was 283 ppb which exceeded the ERM concentration (180 ppb). Toxic effects of PCB contamination are manifest as complex toxic syndromes such as liver and endocrine system dysfunction, immune suppression, teratogenicity, "wasting syndrome," and impaired reproduction (Smith et al., 1990; McConnell, 1980; Poland, 1982; Safe, 1985). Toxicity impacts of PCBs to fish and wildlife species have been reviewed and documented by Eisler (1985). There are 18 PCB congeners that are approximate isosteres of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) and capable of producing a toxic response similar to dioxin in various organisms (Smith et al., 1990; Safe et al., 1982; Safe et al., 1985). Because PCB contamination could pose a potential threat to aquatic resources and overall health of the bay, additional surveys are needed to determine the magnitude and areal extent of this contamination.

G. Dioxin and Dibenzofuran Compounds

Based on the samples from six widely separated stations within the deeper bay, dioxin compounds appear to be widely distributed. Dioxin compounds, polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs), are by-products formed during the manufacture of other compounds and can be found in air emissions or effluents from industry. None of the PCDDs have any known use. Sources of dioxin include the manufacture of chemical pesticides, the most important of which is the herbicide 2,4,5-T (2,4,5-trichlorophenoxyacetic acid). In 1957, dioxin was identified by German chemists as a contaminant in the manufacture of trichlorophenol, a precursor of a variety of pesticides. The use of 2,4,5-T was suspended in 1979, and disappeared from

United States commerce in 1983. However, prior to the ban, 2,4,5-T was used in large quantities. For example, in 1974 about 6 million pounds were used in the U.S. and probably as much as three times that amount worldwide. Dioxin was also found in the herbicide "agent orange" used by the military during the Vietnam War. Agent orange was a 50:50 mixture of 2,4,5-T and 2,4-D (2,4-dichlorophenoxyacetic acid) (Gough 1987). The dioxin congener 2,3,7,8-TCDD is a potent chemical toxicant which serves as the reference compound for a large class of halogenated aromatic hydrocarbons (Poland and Knutson 1982; Safe, 1990).

Dioxin compounds are still introduced into the environment. One of the most important contemporary sources is combustion of modern, synthetic materials. The chlorinated bleaching processes of many paper mills have also resulted in the release of dioxin via industrial effluents. Other sources include the manufacture of polychlorinated biphenyls (PCBs), pentachlorophenol, and polyvinyl chlorides (PVCs).

The dioxin molecule 2,3,7,8-TCDD is the most toxic synthetic compound ever tested under laboratory conditions (Eisler 1986). The PCDDs, as a class of compounds, are stable toward heat, acids and alkalis. Dioxin (2,3,7,8)-TCDD is a hydrophobic (water-fearing) molecule, with a solubility in water of only 0.2 microgram/liter (0.2 part per billion). The PCDDs are chemically stable and decompose only at temperatures greater than 500 degrees C (a situation rarely encountered in nature) or through photodegradation (direct exposure to sunlight) (U.S. Environmental Protection Agency 1988). PCDDs are concentrated in sediments or biota. In sediments (in association with organic matter), dioxin will remain largely unaltered and ingestion by animals can introduce these compounds into the food chain. In mammals, 2,3,7,8-TCDD is readily absorbed through the gastrointestinal tract, and absorption through intact skin has also been reported. After absorption, 2,3,7,8-TCDD is distributed to tissues high in lipid (fat) content; however, in many species, the liver is a major storage site (U.S. Environmental Protection Agency, 1988).

Only two probable sources of dioxin input to St. Joseph Bay have been identified -- atmospheric deposition and discharge via effluent from a local paper mill. No other sources appear probable although potential contributions from urban stormwater runoff, petroleum and/or coal sources, and local industrial operations should be evaluated.

Atmospheric deposition (air pollution) could be a source of dioxin compounds. It is known that extremely small amounts (<6 pg/m^3 range) of dioxin compounds are present in the atmosphere in the United States (Smith et al., 1989; Harless et al., 1990; Maisel et al., 1990; Hunt et al., 1990; CDEP, 1988; Harless et al., 1991; Edgerton et al., 1989; Eitzer et al., 1989; Hunt et al., 1990).

On a volume to volume basis, the concentration of octochlorodibenzo-*p*-dioxin (OCDD) in air is approximately 1 billionth the concentration found in the sediment of St. Joseph Bay. The more chlorinated (and less toxic) isomers of dioxin, such as OCDD, are much more abundant than the less chlorinated (and more toxic) forms, such as TCDD.

The other possible source of dioxin contamination to St. Joseph Bay is the paper mill. This mill discharged industrial effluents directly into the bay from 1937 to the early 1970's. In the mid-1970's, the mill's industrial effluent was re-directed through the City of Port St. Joe's wastewater treatment lagoon. In 1977, the City's effluent discharge to the Gulf County Canal (including the paper mill's effluent) was authorized under an NPDES Clean Water Act permit (U.S. Environmental Protection Agency, 1978). NPDES permits are good for 5-year periods, after which they are re-evaluated by the EPA. The permits are usually re-issued, with or without modifications.

Dioxin limitations were not a part of the earlier permits (1977-1989), but the 1990 permit had an effluent limitation for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin set at 0.4 picograms/liter, effective through September 30, 1995. The permit, reissued in

October 1994, allows the City to discharge industrial and domestic wastewater from a publicly owned wastewater treatment plant (SIC Code 4952) into St. Joseph Bay via the Gulf County Canal, without an effluent limitation for dioxin compounds (U.S. Environmental Protection Agency, 1994). However, water sample monitoring for the seventeen 2,3,7,8- substituted dioxin isomers is required under the current permit.

Biological Hazards Associated with Dioxin and Furan Compounds

Contamination of ecosystems and the species that inhabit them, with chlorinated dibenzodioxin (CDD) and chlorinated dibenzofuran (CDF) compounds, is a primary concern of the Service. Eisler (1986) documented many of the hazards to fish and wildlife associated with exposure to dioxin compounds. Studies in the Great Lakes have demonstrated definite linkages between these compounds and reproductive failures in fish (Ankley et al., 1991), birds (Tillitt et al., 1992; Kubiak et al., 1989), and mammals (Jones et al., 1993). The developmental and reproductive toxicity of dioxin compounds has been extensively described by Peterson et al. (1993).

Early life stages of fish are highly sensitive to dioxin compounds at parts per trillion concentrations (Helder, 1980; Walker and Peterson, 1992). Recent reports for brook trout (*Salvelinus fontinalis*) revealed that the concentration of dioxin (TCDD) in ovaries and spawned eggs was estimated to be 61 and 39% of the whole body TCDD concentration, respectively (Tietge et al., 1998). In a follow-up study (Johnson, et al., 1998) of brook trout, early life stages dosed by maternal transfer of TCDD, the concentration in eggs causing 50% mortality at swimup and at the end of the study was 136 and 127 pg TCDD/gm of egg (parts per trillion), respectively. This is cause for concern because of potentially adverse reproductive impacts to the threatened Gulf sturgeon (a bottom feeding species) or other sensitive fish species. A Gulf sturgeon was captured and released in St. Joseph Bay (Parauka, personal communication) and the species is known to use coastal bays as winter feeding areas.

Dioxins have also been shown to biomagnify. Jones et al. (1993) demonstrated biomagnification of dioxin in adult cormorants, ring-billed gulls and mergansers (range 104-356 pg/g, TCDD-EQ) from habitat sites with sediment toxicity equivalents (range 6.3-14.0) comparable to those observed in St. Joseph Bay. Morphometric brain abnormalities in great blue heron hatchlings have been linked to polychlorinated dibenzodioxins (PCDDs) in British Columbia (Henshel et al., 1993). In addition, dioxins and furans have been linked to reproductive impairment in wood ducks in central Arkansas (White, 1994; White et al., 1995).

Dioxin is a carcinogen and teratogen in rodents (Rier et al, 1993). Impairment of reproductive development has been documented in mammals, including inhibition of spermatogenesis and alterations in sexual behavior (Peterson et al., 1992). Dioxin is one of several chemicals known to have reproductive and endocrine-disrupting effects (Colborn et al., 1993, Mably, 1992a, Mably 1992b, Mably 1992c). It has been linked to increased frequency of endometriosis in rhesus monkeys (Rier et al., 1993). Potential impacts to a marine mammal, the bottlenose dolphin (*Tursiops truncatus*), which uses St. Joseph Bay extensively for habitat and food, is of particular concern.

Although all species assessed are quite mobile (and such mobility could limit their exposure to localized dioxin contaminated areas), and the invertebrates sampled (particularly the shrimp) are short-lived, residues of dioxin compounds were measured in the biota of the St. Joseph Bay ecosystem. Concentrations of dioxin may even be significantly higher in longer living invertebrates (such as the southern quahog clam, a species harvested from the bay) which inhabit deep sediments or in animals such as the Gulf sturgeon, bottlenose dolphin, or loggerhead sea turtle. The concentrations of dioxin measured in biota in this study were below the Federal Food and Drug Administration [FDA] action level for human consumption.

At this time, no particular degree of injury to fish and wildlife species attributable to dioxin contamination of the bay's sediments has been identified. However, any biological uptake of dioxin from the sediment is undesirable. Many subtle effects to biological systems could be occurring as a result of dioxin contamination including the impairment of fish and invertebrate reproductive, endocrine and immune systems. Unfortunately, such effects evaluations were beyond the scope of this study.

CONCLUSIONS

St. Joseph Bay is a unique, high diversity coastal lagoon which receives a minimal amount of freshwater from land drainage. The bay is deep, clear, and highly saline. It supports a wealth of important plants and animals. The State of Florida considers the bay an important public and natural resource. Proper management of this resource should include utilization of all information available.

The St. Joseph Bay Aquatic Preserve Management Plan stipulates that areas in the bay which are "important in maintaining the *productivity* of the Aquatic Preserve contain outstanding resource values, are in need of restoration, *or are important habitat to State and federally designated species,* should receive increased management and protection." (Florida Department of Natural Resources, 1992)

Management of the environmental quality of St. Joseph Bay requires careful consideration of several characteristics of this waterbody. The effects of chemical contaminants on coastal waterbodies depends on the quantities and types of chemicals introduced and the ability of the waterbody to cleanse itself through natural processes. Some coastal systems have a greater capacity to cleanse themselves than other systems. They can therefore assimilate and/or discharge greater quantities of chemicals than can other systems. Coastal water bodies can cleanse themselves through flushing from freshwater inflow, tidal circulation, or storm forces; or breakdown and assimilation of chemicals. However, deficiencies in these cleansing mechanisms exacerbate the introduction of contaminants and environmental damage.

The current study focused on the deeper portion of the bay (> 20 feet) representing approximately 20,000 acres of habitat or roughly 46% of the bay. Therefore, it is the only area of the bay for which management recommendations can be made. Based on available information and the results of this study, we are certain of the following:

1) Vertical amplitude of the tide in the bay is approximately 1.4 feet; substantially less than most estuaries on the west coast of Florida. Consequently, the bay has a minimal tidal capacity to flush itself of contaminated water and sediments.

2) Geological surveys of the bay and evaluation of tropical storm/hurricane data indicate that little change has taken place in the sediments of the bay over an extended period of time. Hurricane activity will have minimal influence on sediments in deep areas of the bay. Therefore, cleansing of contaminants through hurricane activity is unlikely.

3) Inflow of freshwater or introduction of naturally eroded soils from land drainage (i.e., large rivers or creeks) into the bay is insignificant. Therefore, cleansing of bay waters via freshwater inflow and dilution, or burial of contaminated sediments by clean, eroded upland soils, is unlikely.

4) The sediments of the deeper areas of the bay are naturally rich in silts, clays and organic material. These sediments are particularly susceptible to binding and accumulation of anthropogenically introduced chemical contaminants.

RECOMMENDATIONS

In view of the above, stringent management actions are required for St. Joseph Bay. Preservation of the biological productivity and high species diversity of the bay is dependent upon, among other things, the preservation of healthy sediment habitat within the deep areas. Therefore, the following needs, and management actions, are identified.

Research Needs

1. Additional sediment stations should be evaluated to more accurately define and delineate the concentrations, distribution, and temporal changes in un-

ionized ammonia, metals (particularly arsenic and mercury), PAH compounds, PCB congeners, and dioxin and dibenzofuran compounds.

2. Special attention should be focused upon the alkylated PAH compounds to define their individual toxicity to benthic fauna, and the effect of these chemicals on overall productivity and reduction of species diversity.

3. Additional research related to biological uptake of dioxin compounds by other biotic species should be done. Focus should be on sedentary benthic mollusks, demersal fishes such as flounder and long-lived resident species including the brown pelican, bottle-nose dolphin, loggerhead sea turtle and Gulf sturgeon.

Ecosystem Management Actions

1. Incorporate into the goals and objectives of the St. Joseph Bay Committee the goal of creating and implementing a management plan for the reduction or elimination of chemical contaminant loading into the bay. The leadership of a specifically designated chemical contaminant sub-committee is recommended.

2. Modify the St. Joseph Bay Aquatic Preserve Management Plan -- Research and Monitoring Program, to include: a) expanded sampling and evaluation of the chemical quality of the sediments within the bay, including analyses for metals, PAHs, PCBs, dioxins and furans; b) design and implement a statistically valid, areal sediment-quality monitoring program; c) design and implement an aquatic species monitoring program; and d) correlate the observed species diversity, relative abundance and productivity with sediment and water quality data.

3. Develop and implement a strong public education program that includes information about the environmental and economic risks of chemical contamination, and the resource and social benefits associated with the elimination of these chemical contaminants from the environment.

Recommended Actions for Industry

1. Industries should conduct evaluations for all chemicals of concern carried within their point source discharges to St. Joseph Bay and the Gulf County Canal, and in any stormwater runoff entering the bay.
2. Industries are encouraged to eliminate the use of elemental chlorine and chlorine compounds from processes.
3. All smoke stack emissions within 20 miles of the bay and associated particulate discharges (fly ash, etc.) should be monitored for dioxin compounds and other chemicals of concern.

County and Municipal Recommendations

1. Design and implement a stormwater management system for all urban storm waters draining into St. Joseph Bay or its tributaries.
2. Minimize the use of septic sewage systems that drain to the bay by providing public sewage hook-ups.
3. Encourage education and voluntary management actions of county and city citizens related to proper land management and use of farm and residential fertilizers, herbicides and pesticides.
4. Participate in the planning and implementation activities of the U.S. Coast Guard relative to the development of the Northwest Florida Oil and Hazardous Materials Spill Prevention and Response Plan, as it applies to St. Joseph Bay.

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